PHOTOGRAPHIC HANDY-BOOKS.

NO. II.

EMULSION PROCESSES

IN

PHOTOGRAPHY.

BY

CAPTAIN W. DE W. ABNEY, R.E., F.R.S.

LONDON:
PIPER & CARTER, 15, GOUGH SQUARE,
FLEET STREET, E.C.

1878.

P. MEAGHER,

PHOTOGRAPHIC APPARATUS MANUFACTURER.

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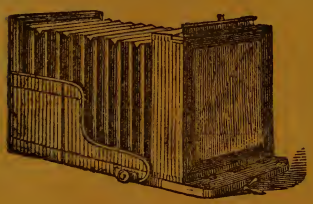

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10 by 8	6 16 0	1 0 0	2 0 0	1 5 0	1 1 0
10 by 10	7 10 0	1 0 0	2 0 0	1 5 0	1 1 0
12 by 10	8 0 0	1 5 0	2 10 0	1 10 0	1 7 0
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PREFACE.

It has been the endeavour of the Author to collect, in the form of a "handy-book," those Photographic Emulsion Processes which have been received with most favour by experienced workers, and with which he is practically acquainted himself; and, at the same time, to give theoretical explanations of some of the phenomena which are met with in these particular processes.

To avoid misconception, the Author wishes it to be understood that much of the original substance of the work, except where special references have been given, has already appeared in the columns of the *Photographic News*, or in papers read before the Photographic Society of Great Britain.

The Author also wishes to make grateful acknowledgment to the Editor of the *Photographic News* for the permission accorded to use several woodcuts which illustrate the work.

PHOTOGRAPHY WITH EMULSIONS.

CHAPTER I.

PRELIMINARY CONSIDERATIONS.

The term emulsion is derived from the Latin word "emulgere," to milk out, and the definition of it as found in the dictionary is, "any milk-like mixture prepared by uniting oil and water by means of another substance." For our photographic technology this is hardly a correct definition, for by it we mean a sensitive salt of silver in very minute division, held in suspension in some viscous body, such as gelatine, or, more commonly, collodion. With the sensitive salts held in the latter we propose to deal firstly, and then to show the peculiarities of, and the difference in its manipulation of the second.

We shall first deal with some theoretical considerations connected with the preparation of the emulsions, and subsequently give the mode of preparing the plates.

An emulsion in collodion in its simplest form, when

required for producing negative pictures, may be considered to be simply pure silver bromide held in suspension in collodion, and so well prepared that when a plate is coated with it, a homogeneous film results; a film which, in fact, is equal in sensitiveness and in physical qualities to any which can be prepared by the bath process.

The reason why silver bromide is chosen in preference to the iodide or chloride is, that the iodide is very difficult to emulsify in collodion which is of such a consistency as shall pour; and that the chloride, if not slower, is less easily amenable to the alkaline method of development than the bromide. The chloride can be emulsified as is well known, but is better adapted for a printing process, and in that respect is without a rival for delicacy. It will be seen, however, that both the iodide and chloride, or both together, are used in emulsions in combination with the bromide; and that when so used they have certain qualities which are said to improve the developed image. We may as well state, at the outset, that in our opinion there is nothing to compare with pure bromide "solus," for general work, but this opinion must be taken for what it is worth.

Collodion emulsion processes are divided into two classes: one in which the emulsion is made up and used without any preliminary extraction of the soluble salts necessarily present in the collodion after the double decomposition of the soluble bromide, &c., and the silver nitrate; and the other where these soluble salts are extracted. In the first process the plates are washed, and then usually receive a coating of some preservative, whilst in the second they are generally left to dry spontaneously,

and are used without any preservative, though it is not uncommon to dissolve resinous matter in the collodion, to act as a temporary varnish. The theoretical value of the preservative we may subsequently allude to briefly, when other matters have been considered.

The plain collodion with which the emulsion is to be made shall be first dealt with, distinguishing the qualities necessary for the unwashed and for the washed emulsion.

Some emulsion workers have laid it down as an axiom that the pyroxyline for the two processes should differ, while others declare that this is unnecessary. Again, some declare that to gain good density the pyroxyline should contain a percentage of organic matter, presumably to be capable of acting on the silver bromide during development, or by forming some definite compound with silver. Our own experience is, that for securing density organic matter is unnecessary, though it may improve sensitiveness; and we have found in some instances that density was absolutely impossible to attain where organic matter was present. We shall touch on the question of density of the image further on.

If a preservative be used as a sensitizer, there can be no doubt that a collodion should be used which is as porous as possible, to enable it to surround the particles of the sensitive salt. This porosity has also another advantage, which is, that when the preservative is washed off previous to development, the sensitive salt is immediately accessible to the action of the developer. It is such a collodion that is recommended for dry plates prepared with the aid of the bath, more particularly in the collodio-

albumen process, though in this process the sensitive salt is more especially contained in the albumen, and it is therefore necessary that a fair quantity of the latter should be on the plate, which is accomplished by this porosity of the collodion film. For any emulsion process we consider a horny collodion objectionable, owing to the difficulty that exists in making the developer penetrate through the film. A horny collodion has, however, one advantage in that it acts as a varnish to exclude the air from the sensitive salts enclosed within it. In the following formulæ which are given for the preparation of pyroxylines, one will produce an ordinary tough film, and the other a fairly porous film, and consequently a rather powdery pyroxyline.

The solvents of the pyroxyline should be as pure as practicable to secure the maximum of sensitiveness, and this has been shown to be the case by that indefatigable experimentalist, Mr. H. Berkeley, in a communication he made to the *British Journal of Photography* during the last year. There is, for instance, no doubt that when methylated alcohol is used, there may be a lack of sensitiveness, and even a production of fog. The ordinary methylated ether, however, will be found, as a rule, to be sufficiently pure.

Effect of a Base upon Pyroxyline.—The general way of forming an emulsion in collodion is to dissolve the soluble bromide, &c., in the collodion, and then to add silver nitrate to it, either in excess, or in defect, and experience has shown that the sensitiveness depends to some extent on the metal which forms a part of the bromide. Mr. Warnerke states that the pyroxyline enters into combination with the

metal, in some instances altering it in chemical, and therefore of necessity in physical, qualities. As an instance, he adduces the action of ferrous chloride on gun-cotton. That such action does take place must be admitted, but up to the present time we have no researches which point out what those changes are. It must also not be forgotten that some of the haloids enter into combination with alcohol; good examples of this are to be found in calcium chloride and zinc bromide, the latter salt entering into combination with a considerable evolution of heat. It is highly probable that this compound may re-act on the pyroxyline which is in solution, but from analyses which have been made it seems that the metallic base does not enter into absolute combination. In one case, which was brought under the notice of the writer by Mr. Warnerke, the pyroxyline in solution had been in contact with a copper salt, and a blue colour was noticeable after the pyroxyline had been desiccated, but this would seem to arise from the traces of the insoluble form of salt which nearly always accompanies this particular bromide (see page 9). The caustic properties of silver nitrate, too, will probably affect the pyroxyline, and it will be noticed, in some of the processes described, that the contact of the silver salt with the collodion is insisted upon strongly. The writer's own experience is, that not much benefit is derived from such contact, but undoubted authorities on the subject have prescribed it.

The Cause of Fog in Emulsions.—Every student in emulsion work has found, and will find, that the chief obstacle that he has to overcome is the tendency for the

plates prepared with it to fog on development, and it has taken a great deal of experimental work to enable it to be overcome. The reason of the fog-giving emulsion has been obscure; but the writer ventures to think that the very recent researches that have been made on the subject have explained in a great measure, if not entirely, its *raison d'être;* and, in spite of being tedious, or of being told that the reader knows all about it, a summary of what is known of the matter is appended.

Setting aside the collodion from the question, and merely taking into consideration the sensitive salts employed, we may arrive at very definite results. It has been asserted that a neutral combination between two substances can never take place; for example, if we mix potassium chloride with silver nitrate we shall never be able to get pure silver chloride, however much we may wash it—that either the soluble potassium or silver salt will always be in excess, though in the minutest quantities. This certainly is the case theoretically, because do what you will, and wash as long as you like, there still must be some infinitely small part of the soluble salt left behind. Now for ordinary chemical reactions, where the products of these combinations have to be weighed, the residual impurity may be inappreciable, being so infinitesimal that no balance yet constructed can show them. Though a balance may be inoperative, yet, as is well known, light is able to show us impurities in a substance which may not be one millionth part of a grain in weight. By passing the light from the heated vapours of the substance and its impurity through a prism, and noting its spectrum, we may be able to detect the latter.

The spectroscope will not tell us at present, however, whether the silver or potassium is present as nitrate, chloride, bromide, oxide, &c.

The question now arises, is it possible to detect this? Is it possible, for instance, to say whether any infinitesimal quantity of oxide be present? In the majority of cases the question would be an open one; but where we are dealing with silver salts which are sensitive to light, and which are amenable to development, we think we can give an affirmative answer. Sometimes, however, the impurities in the bromides can be shown by weighing. For, in a paper read before the Photographic Society of Great Britain on the 8th of February, 1876, Mr. Warnerke stated that on testing the different bromides, he found that considerable variation from the theoretical quantities necessary to combine with silver nitrate was observable. Thus he found that one grain of silver nitrate requires

Of potassium bromide	1·35	grains,	theoretically,	1·429	grains,
Of ammonium bromide	1·80	,,	,,	1·78	,,
Of cadmium bromide	1·005	,,	,,	·885	,,
Of zinc bromide	1·43	,,	,,	1·59	,,

The cadmium salt, he states, was not anhydrous, therefore this may account for one discrepancy; the potassium and zinc point to the presence of oxide, whilst the ammonium seems to indicate the presence of free haloid. Be this as it may, a careful experimenter has found these discrepancies.

Let us see how potassium bromide may be contaminated in its preparation. We find that the mother liquor from

the sea water brine is treated with chlorine, and that this takes the place of the bromine in combination with the magnesium; the yellow liquid is agitated with ether, which takes up the bromine, and this ethereal solution is treated with potash in solution. The bromine forms the bromate and bromide of the alkali, and when the alkali is nearly saturated, it is decanted off and further treated. Now, from what we have said before, it is more than probable that the bromide is contaminated with the alkali, however well it may be separated: the traces of alkali may even be so small as to be undetected by litmus paper.

Again, the bromides of the alkaline metals are prepared by acting on the alkalies with an excess of bromine, a similar reaction to that above taking place. The bromate is decomposed by ignition, and this heating alone tends to decompose the bromide, in which case we should have the oxide of the alkali left behind. In good preparations it would be excessively small, but still sufficient, for the purpose we shall indicate presently.

The bromides of the metals may be similarly contaminated. Take zinc as an example; the metal is easily oxidized, and the zinc oxide is soluble in zinc bromide, as it is in the chloride. In all these cases, then, it is possible we may have traces of oxide with the bromide. Again, there are some metals which form two bromides, as that of copper; and experience shows that it is very hard to get the compound fully saturated with bromine without having part of it in the less saturated state.

If such bromides, contaminated with the oxide, or containing the lower combination of bromine, be brought in contact with silver nitrate, we shall have two separate

reactions to consider. In the case of the oxide contamination, when silver nitrate is in excess, we shall have—

Potassium bromide, Potassium oxide, and Silver nitrate

$$x\,KBr + K_2O + (x+2)Ag\,NO^3$$

Give Silver bromide, Silver oxide, and Potassium nitrate

$$= x\,Ag\,Br + Ag_2\,O + (x+2)\,K\,NO_3$$

Or, besides the silver bromide, we shall have silver oxide formed.

In the case where we have a sub-bromide of the soluble metal formed, we have, taking copper as a sample—

Cupric bromide, Cuprous bromide, and Silver nitrate

$$x\,Cu\,Br_2 + Cu\,Br + (2x+2)\,Ag\,NO_3$$

Give Silver bromide, Silver sub-bromide, and Cupric nitrate

$$= 2x\,Ag\,Br + Ag_2\,Br + (x+1)\,Cu\,(No_3)_2$$

Or, we have silver sub-bromide formed; if it be preferred, this compound may be supposed to be made up of silver bromide and metallic silver ($Ag_2\,Br = Ag\,Br + Ag$), though from experiments already published, we have proved it to be the sub-bromide.

Evidence of the most unmistakable character points to the chemical theory of the formation of the photographic image—evidence so strong, and so well known, that it would be out of place to record it here. Briefly we may say that the action of light on a silver haloid seems to be to reduce it to a simpler type, which we may call the sub-haloid. Thus

Silver bromide gives Silver sub-bromide and Bromine.

$$Ag_2\,Br_2 = Ag_2\,Br + Br.$$

If this be admitted, we can proceed a step further; but if

not, the subsequent argument falls to the ground. If any reader will not admit it, he should read all the various evidence that has been adduced since the time when Scheele first made his experiments with silver chloride, and we doubt if he can remain unconvinced, more particularly in regard to the visible image formed on the bromide and chloride. It is a pertinent question to put, as to whether the visible and the invisible (or developable) image are of the same nature; which may be answered by another question : Can the line be drawn where the image is invisible? If so, what is the boundary between the two? If we admit the theory of the formation of the visible image, it seems hardly logical to deny a similar formation for the invisible or photographic image. It is quite possible that beings with more acute sight than ourselves might be able to see the image which we cannot, as we know certain insects can hear sounds which do not affect our auditory nerves. Coloured particles are visible when put together *en masse*, but if only a few coloured particles are present in a mass of colourless particles, it is quite certain that they may remain undetected.

If we may, then, be allowed to beg the question, or rather to assume that silver bromide is reduced by light to the sub-bromide as indicated, the following explanations may be proceeded with.

We have seen that we may have oxides and sub-bromides contaminating the bromides, and in a similar way we may have oxides and sub-chlorides contaminating the chloride. In a communication to the *Philosophical Magazine*, which was reprinted in the photographic journals, the writer showed that it was possible

to develop an image on a film never exposed to light, but which was in contact with a film (during the operation of development) on which an invisible image had been impressed. The explanation there offered seems every way to meet the requirements of the case, which is, that where a nucleus, if it may so be termed, exists, there the silver from the adjacent bromide will be deposited in preference to any other part of the film. Such a nucleus is found in the silver sub-bromide or sub-chloride obtained by exposing a plate to light. However produced, we may assume it will act in a similar manner.

The case of the oxide is not so clear; but a little experiment will throw light on it. Prepare silver oxide as an emulsion in collodion; dissolve (say) 6 grains of silver nitrate in an ounce of plain collodion, and add to it 2 grains of potash in alcohol. This will give an emulsion of oxide of silver. Now wash it, and treat it as a washed emulsion, and add a drachm of it to an ounce of a washed emulsion which works perfectly free from fog; coat a plate, and develop it. It will be found that inevitable fog is produced. In this case the silver oxide (presumably partially reduced to the metallic state, since the oxide is an unstable compound) acts as the nucleus on which the silver bromide is reduced to the metallic state by the alkaline developer.

It must be borne in mind that the invisible image must necessarily be composed of very minute particles of the altered silver salt. If, then, such a small number of particles distributed over a film are sufficiently powerful to form nuclei for the development of the image, the same minute quantity of oxide, or chemically produced sub-haloid of silver, might be capable

of producing the same results. The above, then, seems to be the explanation of fog in emulsion plates. Now as to the remedies.

On the Elimination of the Causes of Fog from Emulsions. —It is well known that when we have an excess of soluble haloid, freedom from fog is secured. In some recent experiments we carried out, we found that silver bromide is formed before any other silver compound, except the iodide, when the sensitive salt is formed from haloid salts, and not from the halogens themselves. Thus, if potassium bromide be contaminated with potash, we shall have both silver bromide and silver oxide formed, if an excess of silver nitrate be added; but if there be a defect of the nitrate there will not be a trace of silver oxide, but only silver bromide. Again, if we take bromide of copper, which is usually contaminated with the sub-bromide as already stated, it will be found that the bromide is all utilized before the sub-bromide is attacked at all; and if, in addition to the bromide, we have a metallic chloride present which may be contaminated with sub-chloride, the order in which they will combine with the silver nitrate is,— bromide, chloride, sub-bromide, sub-chloride. Thus, if there be only sufficient silver nitrate added to an emulsion to combine with the two first on the list, the other two will be left in the emulsion as harmless compounds. The *rationale* of the elimination of fog from the finished emulsion in which there is *at first* an excess of silver nitrate is thus demonstrated. We have now the theoretical explanation of Major Russell's statement that a little soluble bromide must be left in the film when silver bromide is formed by the bath in the usual way, and it may be remarked,

parenthetically, that whether the image be developed by the alkaline or acid methods, the same result must hold good. Supposing we have an emulsion which contains bromide, sub-bromide, and oxide of copper, and also a slight excess of silver nitrate. The addition of certain metallic chlorides or of hydrochloric acid will at once convert the sub-bromide and oxide into the chloride of silver, leaving harmless compounds behind: the metallic chlorides which are of use are those which readily part with chlorine, and which, therefore, preferably form more than one chloride, such as copper, cobalt, gold, platinum, &c. When other chlorides, such as of the alkalies, are employed, the needful substitution may not take place, because the affinity of the alkali for the chlorine is greater than for the sub-bromide; and therefore the elimination of the sub-bromide is not effected. Thus, if all the silver nitrate in original excess be converted into silver chloride, we have the silver sub-bromide to get rid of. Now, supposing we are using sodium chloride as a corrective, then we should have

$$Ag_2\,Br + NaCl,$$

which can form no new saturated silver compound, since an atom of metallic silver, sodium, bromine, or chlorine cannot be left in a free state; but if we use (say) cobalt chloride, we have—

$$Ag_2\,Br + CoCl_2, \text{ which can form—}$$
$$Ag\,Br + AgCl + CoCl.$$

The CoCl, or sub-chloride of cobalt, is harmless, and can be washed out of the film.

It will, therefore, be seen how it is that addition of these chlorides to a washed emulsion will give freedom from fog.

Secondly, if an excess of silver nitrate be used, it is

evident that something else besides a mere chloride will be required, since the sub-salts and oxides may be formed. This we find in the employment of an acid, or of a halogen itself, or both together, added to the collodion, and to be most rapidly effective. Whatever is used is best added to the soluble salts before the silver nitrate is added.

Suppose nitric acid alone be employed, then any oxide or carbonate will immediately be attacked, as also any of the sub-bromides—such as of copper. Again if aqua-regia be employed, we know that chlorine is evolved in an extremely nascent state, and that this would attack either oxide or sub-bromide, fully saturating the unsatisfied atom in the latter. If, now, silver nitrate be added, silver bromide and chloride would result with some compounds (perhaps such as the chlorate), which would be as inert as producers of fog as the silver nitrate itself.

If a halogen be employed without any acid, the same result would occur. Thus, suppose we had as impurities an oxide and a sub-bromide, and that we added a solution of bromine to it, we should get the oxide changed to a bromide and bromate (the latter salt of which is experimentally proved to be inert), and sub-bromide changed to a bromide.

If the halogen be added last, when there is an excess of silver, it is probable that until all the latter is converted it will exert no unfogging action; but if an acid, such as nitric acid, be added, it will exert its proper influence, though slowly; for it will convert any oxide or compounds of the oxide into nitrate, and from the silver sub-bromide dissolve away the loose atom of silver, converting the sub-bromide into bromide and nitrate. Thus:—

$$4Ag_2Br + 6HNO_3 = 4AgBr + 4AgNO_3 + N_2O_3 + 3HO.$$

Or, at all events, a fresh combination will be made, which is unacted upon by the developer.

There is also a method of eliminating fog from the dry plate when it is coated, without doctoring the emulsion at all. This need not apply only to washed emulsions, but it can be effected during the washing of the plates prepared by the unwashed emulsion. In addition to the elimination by the acids, and by the metals forming two bromides or chlorides, we can further effect it by using a solution of potassium bichromate, permanganate of potash, or per-oxide of hydrogen. The reason of this seems to be due to oxidation; the cause at present is somewhat obscure, but the writer is engaged in experiments as to the cause. It may be, in the first case, that a minute quantity of silver bichromate is formed by the oxide, or that the free silver atom of the sub-bromide is oxidized, and then formed into silver bi-chromate; with the second it may be that the manganese salt is substituted for the silver salt, and is inert; and in the last case it may be that the silver salt is per-oxidized, and forms an oxy-bromide, which is un-affected by the developer. This seems probable, since ozone has the same effect on the fog.

It may not be uninteresting to note an experiment which throws some light upon this point, though it is not conclusive. If a plate be coated with emulsion, and be allowed to thoroughly darken in the daylight, and then drops of these destructives be placed on the film, and allowed to act for a few minutes, it will be found, after washing, that the spot where the bichromate and the hydrogen peroxide have been dropped the colour and appearance of the film remain unaltered. Where the manganese has been, the film is slightly brown. Now it

the film be treated with sodium hyposulphite, the parts where all the three have been will become transparent, showing that everything, except the collodion, has been dissolved away, whilst on the rest of the plate there will remain a delicate layer of metallic silver.

Be the theory what it may, the treatment holds good. Perhaps the application of nitric acid is the safest, but to that we shall refer later on.

Density of the Film.—In securing the sensitiveness of a film, and resulting intensity of the developed image, there are two points which must be considered :—1st, the opacity of the film ; and, 2nd, the method of development.

Density of a film, it will be seen, is an absolute necessity to secure the maximum of sensitiveness, since if a film be not opaque to the rays of light which are useful for forming the invisible image, there must be a loss equivalent to the rays which pass through. Some of the processes, therefore, which give transparent films probably owe their insensitiveness in a great measure to this fact. But it must be borne in mind that there are some rays which may be allowed to pass through, and which will yet cause no loss in this direction. Thus, for photographic work generally, we may say that the blue rays are the active ones. If, therefore, by any means, we can stop all these rays from passing through, we may allow a transmission of yellow and red rays without diminishing the sensitiveness. Again, if we mean to develop plates by the alkaline or ferrous oxalate developer, where the supply of silver is derived from the film itself, we are bound to take into consideration the amount of silver necessary to give opacity to the developed image in the highest lights. Practically, it is found that if, over every

square inch of plate, there is four and a-half grains of metallic silver, this is attained; anything less, therefore, would give a lack of density, anything over would tend to give harsh negatives. This consideration applies only where no subsequent intensification is carried out. Fortunately, the densities necessary to secure opacity to the blue rays, and to give sufficient opacity to the image, are found to be coincident.

From what has been said, it will also be evident, theoretically, that with a given amount of silver bromide we are likely to get most sensitiveness if the film, when examined by transmitted light, transmits the red rays; and this is the case as proved by experiment. A film transmitting red rays is much more sensitive to the blue rays than one which transmits all colours, though, for obtaining sensitiveness to the red rays, and these alone, of course the more red light absorbed the better. As at present these are not the rays which photographers look to, we may take it that the red transmitting films are the most useful for ordinary work. Now, mathematical investigation teaches us that if we split up silver bromide into particles, so as to transmit red light when held in a film, that they are of a smaller size than if they are divided so as to transmit blue light through the film. Hence, for a given thickness of film, more of the former would be affected by the incident light than of the latter, and the probabilities are that the reduction of the sensitive compound to the metallic state would take place to a greater extent in the former than in the latter. In the writer's experience this is the case. It is always more difficult to secure density with a film that transmits blue light than with one which transmits red.

Preservatives.—Preservatives, as they are called, are useful in two ways:—The first is, that they act as absorbents of the halogen liberated by the action of light on the sensitive salt; and the other, that they preserve the film from atmospheric agencies. We have already said that recent experiments tend to show that a developable image can be destroyed or become undevelopable by becoming oxidized; hence, if the preservative contain any substance which is more readily oxidized than the image, it will keep the latter from being destroyed by time, as long as the former remains unsaturated with oxygen. This being so, we may expect that a plate having a preservative on it of a proper character will preserve the image for a longer time than one in which no preservative is used. In some instances this is the case, but we have to take into account that the preservative takes up the halogen expelled from the sensitive salt, and is in immediate contact with the image, and if it readily absorb oxygen it will also readily give up the halogen. In other words, we have to strike a balance between these actions to get a film which will retain the impressed, but not developed, image upon it.

Theoretical Considerations of Development.—It will be seen in the directions for developing the emulsion plates, that when the plate has been coated with simply washed emulsion, or when the preservative is soluble in alcohol, that it is recommended that the films should be flowed over with spirits of wine. With the first this softens the film, swelling up the pyroxyline, and allows the developer access to the interior of it. With the latter it dissolves the preservative. It is not an experiment thrown away, if half of a washed and exposed emulsion plate

be flowed over with alcohol, and be then washed and developed. The difference in the rapidity of development, and in the density of the image, on the two halves of the plate will be found to be in favour of that half to which spirit has been applied.

Colonel Stuart Wortley first brought to notice the immense advantage that a strong alkaline developer possesses over weaker solutions in bringing out the invisible image, and at the same time giving greater density to it.

From chemical analogy it may be assumed that the attractive force of the particles altered by light is most vigorous when freshly formed, and that metallic silver also has the same energy of attraction when it is freshly deposited, though it seems probable that in development there is a state in which the sensitive salt can be placed in which it loses its power of development in a great measure. With the weak alkaline developer the silver is reduced but slowly from the bromide, and hence it becomes less "nascent," if we may use the term, than it is when it is rapidly reduced, and when the next particle to it is also rapidly reduced and ready to bind itself to the silver just deposited. Slow deposition of silver is also not conducive to density (as we know by experience when silvering mirrors), and this alone points to the advantage of an energetic developer. Again, from chemical analysis of the developer after it has been used, it is found that a weakly alkaline solution is only capable of reducing about one-third the amount of the bromide that a concentrated solution is capable of reducing.

It will be noticed that the alkaline developer is nothing more or less than a silvering solution, minus the silver, as used for silvering mirrors, the pyrogallic acid taking the

place of grape sugar or sugar of milk. The reduction of the bromide to the metallic state is effected in the same way that the reduction of the ammoniacal solution of silver is effected. The question now arises, Why does reduce it on the part most acted upon by light? The answer is, that unless the developer be restrained by a soluble bromide, or some other similar substance, the film will be reduced all over its surface. What part, then, does the bromide play? This is a question easily asked, but by no means so easily answered. Without entering into any elaborate proof, it seems that the silver bromide is capable of forming a compound with the alkaline bromide, which the sub-bromide cannot do. The former is apparently unattackable by the alkaline pyrogallic acid solution.

The action of the ferrous oxalate developer is probably the same as that of the alkaline pyrogallic developer, though at present, so far as the writer knows, no investigation has been published on the subject. The iron is probably an absorbent of bromine liberated by the reduction of the silver bromide to the metallic state.

CHAPTER II.

PREPARATION OF THE PLAIN COLLODION.

PYROXYLINE.

THE following formulæ for the preparation of the various kinds of pyroxyline will be useful to note. The first is taken from "Instruction in Photography," and is reprinted here as being convenient for reference. "The general directions given are those found in Hardwich's Photographic Chemistry.

1st Process.

Take sulphuric acid (1·842) at 15° Cent.	18	fluid ounces	
Nitric acid (1·456)	6	„	„
Water	4¾	„	„
Or,			
*Sulphuric acid (1·842)	18	fluid ounces	
Nitric acid (1·45)	6½	„	„
Water	4¼	„	„

The water is first poured into a strong glazed porcelain basin, the nitric acid next added, and lastly, the sulphuric

---

* The nitric acid of the strength given in this formula is cheaper than that of the first, and is a standard strength, hence it is recommended for economy's sake to use it.

acid. The mixture is well stirred with a glass rod. The temperature will now be found to be somewhere about 190°. It must be allowed to cool to 150°, and this temperature must be maintained on a water-bath. A dozen balls of cotton-wool, weighing about thirty grains (which have previously been well washed in carbonate of soda and thoroughly dried), should now be immersed separately in the fluid with the aid of a glass spatula. Each ball should be pressed separately against the side of the basin, till it is evident that the acids have soaked into the fibre. Care must be taken that each one is immersed at once. Failing this, a different chemical combination takes place, and nitrous fumes are given off, and the success of the operation is vitiated. Immersing the dozen balls will take about two minutes. The basin should after this be covered up for about ten minutes.* At the expiration of this time the whole of the cotton should be taken up between two glass spatulas, and against the sides of the clean porcelain capsule as much of the acids as possible should be squeezed out. The cotton should then be dashed into a large quantity of water, and washed in running, or frequent changes of, water for twenty-four hours. Finally, when it shows no acid reaction to blue litmus paper, it is dried in the sun or on a water-bath.

2nd Process.

Sulphuric acid (1·842)	6 fluid ounces
Dried nitrate of potash	3½ ounces (Av.)
Water	1 fluid ounce
Best cotton wool	60 grains

* This prevents the access of the air to the fluid, and prevents the absorption of oxygen, and consequent formation of the nitrous fumes.

Mix the acid and water in a porcelain vessel, then add the nitrate (which has previously been dried on a metal plate to about 250°, and then pulverized) by degrees, stirring with a glass rod until all lumps disappear, and a transparent viscous fluid is obtained. This will occupy several minutes.

The whole of the cotton wool must now be separated into balls the size of a walnut, and immersed as stated in the first process, care being taken that the temperature is kept up to 150°. The cotton is then left ten minutes, and washed as before. Mr. Hardwich states that the chances of failure in this process "are very slight, if the sulphuric acid be sufficiently strong, and the sample of nitrate not too much contaminated with chloride of potassium." If failure occur through the cotton dissolving in the acid, a dram less water must be used.

In both processes the operation may be conjectured to be successful if the cotton tear easily in the hand, and if the original lumps cannot be easily separated. Should nothing but fragments of the lumps be detected, it is probable (if the acid used have been of the strength given above) that the temperature has been allowed to fall. If dried, the pyroxyline should, when pulled, break up into little bits, and should not resemble the original cotton in texture.

The weight of good pyroxyline should be greater than the original cotton by about 25 per cent.

If the acids used are too strong, the pyroxyline will be much heavier than this per-centage, and will make a thick glutinous collodion; whereas, if the acids have been too diluted, it will probably weigh less than the original cotton, and will yield a collodion adhering firmly to the

plate, and giving negatives of too great softness; any small particles of dust that may fall on the glass will form transparent marks. The formula given steers between the two extremes. There is a large proportion of sulphuric acid in the above solutions of acids, and it is to this that is probably due the tough film which the resulting collodion gives. In fact, the excess of sulphuric acid partially "parchmentizes" the cotton.

In the next formulæ the proportion of sulphuric acid is diminished, and in consequence we get a pyroxyline which is, if anything, deficient in tenacity. For dry plate processes with the bath, however, it is excellent, and will be found of great use in emulsion processes in which a preservative is used. The formulæ are those given by Warnerke in a communication to the Photographic Society of Great Britain made in 1876.

"When, some time ago, Colonel Stuart Wortley communicated to me his plan of gelatinizing pyroxyline, I immediately tried it, and very soon became convinced that the addition of gelatine supplied a much-desired want. My *modus operandi*, according to the Colonel's formula, is the following:—100 grains of the finest cotton-wool are put into a porcelain jar, and 30 grains of gelatine dissolved in the smallest amount of hot water, are added. By pressing it with a wooden stick, all the cotton will be uniformly impregnated. It is subsequently very thoroughly dried before the fire.

Nitric acid (sp. gr. 1·450)...	... 4 fluid ounces
Water	... 12½ drachms
Sulphuric acid (sp. gr. 1·840)	... 6 fluid ounces

are mixed in the order named. An arrangement is pro-

vided to keep the temperature of the mixture uniformly at 158° Fahr. The dried gelatinized cotton, weighing now about 130 grains, is immersed in the mixed acids, and left in twenty minutes. After the lapse of this time the acids are pressed out, and the pyroxyline quickly transferred to a large vessel of water. Washing and drying follow. Colonel Stuart Wortley recommended also a second mode. Gelatine, instead of being added to the cotton, is dissolved in the water figuring in the formula of the acids, and ordinary dry cotton immersed in the mixture of gelatinized acids. In my experiments I found that a considerable quantity of the acids was left from the first experiments. I added to it 3 fluid ounces of sulphuric acid, and immersed in this new mixture, keeping it at 158°, 50 grains more of dried cotton. Supposing that some gelatine would be dissolved from the first immersion, I imagined it would give me a result approaching to the second of Col. Wortley's formulæ. The weight of the pyroxyline No. 1 was 130 grains, an increase of 30 per cent.; it was not powdery. Ordinary cotton, under similar conditions, decreases 5 to 15 per cent. in weight, and is extremely powdery. The new pyroxyline dissolves perfectly in sulphuric ether (sp. gr. 0·720) alone; it partly dissolves in hot methylated alcohol (sp. gr. 0·815). In equal proportions of ether and alcohol it is soluble without any residue. A solution of ten grains of pyroxyline per ounce of solvent is quite fluid, and the film produced rather strong. The colour of the collodion in a large bottle, unlike ordinary, which is yellowish, is now a whitish opal. The gelatinous precipitate occasioned by the addition of aqua-regia is more difficult to redissolve than in ordinary collodion.

"For comparative trials, bromo-iodo-chlorized emulsions

with excess of silver, and bromized with excess of bromides, were prepared from the new and five other samples of pyroxyline. Before washing, a remarkable increase of intensity and sensitiveness was obtained in the gelatinized emulsion. After washing, the difference was less striking, but still sufficiently marked to prove the new pyroxyline to be a very decided improvement. Sample No. 2, from the remaining acids, was more powdery, but gave negatives less intense.

"I complete these remarks on pyroxyline by mentioning that some time previously I found that pyroxyline giving extraordinary density can be prepared from the raw hemp; and I suppose that the mucilage cementing the fibres, and in many respects resembling gelatine, is the acting agent, performing the very same function in the pyroxyline. Collodion from hemp-pyroxyline is red in colour, and very fluid; but the insoluble deposit is very considerable; it also requires stronger acids. It is worth remarking that the strength of acids must vary with different samples of fibres, even in the case of different cottons. I also prepared very good pyroxyline from Whatman's hand-made paper, which, being sized with gelatine, offers a ready-made material, suitable for making gelatinized pyroxyline."

The great difficulty in this formula is the easy solubility of the cotton at the high temperature. A reduction in the amount of water will prevent this. *Pyroxyline from ordinary cotton can be prepared by the same formula*, and gives a powdery film. The writer disagrees with Mr. Warnerke as to the desirability of this state of the film for washed emulsion when used on rigid supports, such as glass, but the limpidity given by it to the collo-

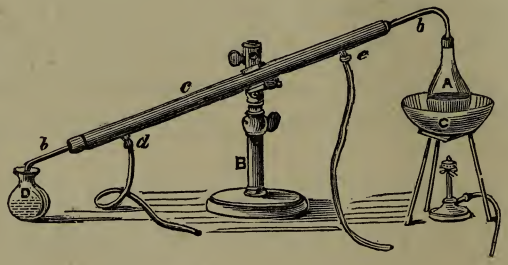
dion is very desirable in the case of a flexible support, such as that with which Mr. Warnerke's name is associated. The amateur will probably find it most convenient to purchase ordinary pyroxyline from some respectable dealer, who is a manufacturer of good collodion, instead of making it himself, more especially as it will be seen that subsequent treatment will render it of any quality that may be desired; for of all processes connected with photography, that of making pyroxyline is, perhaps, the most unpleasant and hurtful to the health and clothes. The stains on the latter from nitric acid or sulphuric acid can never be eliminated, unless the acid be immediately neutralized, and sulphuric acid will rapidly eat through any organic texture, unless it be either washed *thoroughly* or an alkali be applied.

Plain Collodion.—There is nothing to say as to the plain collodion to be made for the unwashed emulsion, excepting that trial must decide which is the best amount of pyroxyline to have in the solvents. It is certainly better to have too much than too little, and half or more of the alcohol should be kept out for the solution of the bromides, and the silver nitrate. If the pyroxyline be insufficient, especially when the emulsion is first made, it will be found that it is almost impossible to secure density of image, and the silver salt will readily settle to the bottom of the bottle.

For the washed emulsion it is advisable to dissolve double the amount of cotton required for the finished collodion, as before, keeping back half of the alcohol of this. It is economical, and certainly not detrimental, to the emulsifying of the bromide.

As regards the character of the solvents there is little to be said in regard to the ether. That of a specific gravity of ·730 is generally employed, and if it be, an alcohol of low specific gravity should be employed, such as ·812; whereas if the ether have a specific gravity of ·720, a specific gravity of ·820 for the alcohol is allowable.

A Liebig's condenser is a very useful piece of apparatus for rectifying the alcohol, but it requires certain precautions to be taken to ensure safety. The apparatus arranged as in the accompanying figure is suitable for the purpose.



The condenser consists of two parts: first, a straight glass tube (*b*), bent at the ends, to which the flask is attached; and second, a jacket (*c*) surrounding the bulk of the tube as shown in the figure. The jacket has two short tubes (*d* and *e*) connected with it, *d* being that through which the cold water is supplied to the jacket, and *e* that through which the warm water is forced out. A couple of india-rubber corks are bored to fit the central tube and to close the ends of the larger tubes. The condenser can be held by a clamp, B. The cold water can be supplied from a water tap, a pinch-cock being used on the india-rubber tube from *d*, so as to allow a very

small flow; or it may be supplied from a jar with a syphon arrangement, if care be taken to keep the bottom of the vessel above the highest end of the jacket. For distilling alcohol, the flask should be held in a metal bowl, C, filled with water, but the bottom of the flask should not touch the bottom of the bowl, otherwise there is danger of bumping and fracture of the former. In practice, we have found that a ring formed by blotting-paper is sufficient protection to the flask. This is placed in the bowl, and the flask placed upon it. A jacket may surround the source of heat, which may be a spirit-lamp, a gas jet, or an oil lamp, but is unnecessary when there is no draught in the place where the distillation is being carried on. The alcohol distils over, and is condensed in the tube *b*, and drops into the flask D. It is not absolutely necessary that the flask should not come in contact with the flame of the source of heat, but it is safer not to allow it to do so.

If we have alcohol of (say) ·830 specific gravity (a very common one, by-the-by) and we wish to rectify it, the best method is to place in the bottle containing it sufficient freshly burnt unslaked lime to completely saturate the spirit, leaving, in fact, very little liquid above the sediment after standing two or three days; this mass must be put in the retort, and the distillation proceeded with. The distilled spirit will be found to be of a specific gravity of ·795. An anhydrous spirit of this specific gravity is very useful to have in stock, as it enables water to be used in the operations of making emulsions without exposing the film to the evil of crapiness. The spirit may be distilled till the lime appears quite dry, for the latter will hold the water

in combination at a temperature far beyond the boiling point of water.

If spirit be distilled from alcohol containing about half as much lime as indicated above, it will be found that the specific gravity of the distillate will be about ·812, which is a very convenient mixture of alcohol and water.

After the plain collodion is mixed it should be allowed to settle. No matter what pyroxyline be employed, it will invariably be found that there is some flocculent matter, too fine for filtering out, which, if not got rid of, will subside after the collodion has remained undisturbed a week or two. In the opinion of the writer this sediment is one great cause of spots on emulsion plates, and therefore every effort should be made to prevent its finding its way into the emulsion.

CHAPTER III.

PREPARATION OF AN EMULSION.

It is unnecessary to enter into the history of the emulsion processes, as it would raise many points of controversy into which the writer has no wish to enter; but it may not be uninteresting to note that the first published formula was by Messrs. Bolton and Sayce in September 1864, in which the collodio-bromide emulsion is made as follows:

Alcohol	½ ounce
Ether	½ „
Bromide of cadmium and ammonium	3 grains
Pyroxyline	2 „

In order to sensitize this, four grains of silver nitrate were added after solution in the minimum quantity of water.

This was shortly afterwards improved by Mr. Sayce, when we find that the formula was—

Collodion...	1 ounce
Bromide of cadmium and ammonium	6 grains
Silver nitrate	10 „

This last formula seems to be that on which all subsequent improvements have been based.

Though not following an historical order, we have thought it best to give the method of preparing an emulsion which can be followed in nearly all modifications of the process; and to make it clearer, a definite formula has been made use of giving an emulsion which is very simple and clean working, and though not boasting any extraordinary sensitiveness, is yet more sensitive than any bath dry-plate process with which the writer is acquainted.

The plain collodion is made as follows:—

Alcohol ·820	... 10 ounces
Ether ·730	... 20 „
Pyroxyline (ordinary)...	... 480 grains

We will suppose that we are going to prepare an emulsion which will make up to twenty ounces. When it is evaporated, washed, and re-emulsified, each ounce of washed emulsion should contain about 6 grains of pyroxyline, and, therefore, we must take one-fourth of the collodion made up as above, which will be $7\frac{1}{2}$ fluid ounces. It is proposed that each fluid ounce of re-dissolved emulsion shall contain about 15 grains of silver bromide. The salt we propose to use is zinc bromide, and we find that about 10 grains of this salt is necessary for this purpose. To our $7\frac{1}{2}$ ounces of collodion, therefore, we must add at some time or another 200 grains of this salt. Two portions of 100 grains each are weighed out: one is dissolved in the smallest quantity possible of alcohol, and 4 or 5 drops of concentrated nitric acid are added to it to get rid of any oxide or other impurity that may be present. This is then added to the collodion.

The other 100 grains are similarly dissolved, but a larger proportion of nitric acid added, viz., 10 drops. This is kept in a test-tube ready for use. We next require 300 grains of silver nitrate to saturate the zinc-bromide, and to allow 3 grains in excess for each ounce of the concentrated collodion. As this will probably be about 11 ounces by the time the additions are made, 330 grains of silver nitrate (which has previously been pounded up in an agate mortar, or the crystals of which have been crushed with a glass stopper on a thick glass plate) are weighed out. This amount is then placed in a large test-tube, with 5 dr. of water, and warmed: a perfect solution ought to result. Ten drops of nitric acid are next added to it. In another test-tube $1\frac{1}{2}$ ounce of alcohol (·820 to ·830) are boiled, and poured upon the dissolved silver. The two fluids may not mix at first, but by pouring them from one test-tube to another this is readily accomplished. The collodion is now placed in a glass jar, and a stirring rod placed ready to hand. It is usually insisted that the subsequent operations should be conducted in the dark room. This exclusion of light is quite unnecessary (as the writer has practically proved), owing to the presence of the nitric acid, which renders the subbromide inert as fast as it is formed by the action of light. The test-tube containing the silver is now taken in the left hand, and the stirring-rod in the right, and three-quarters of the silver nitrate solution is poured, drop by drop, into the collodion, which is kept in brisk agitation by the glass rod. The silver solution is then placed on one side, and the dissolved bromide solution taken in the left hand. All the latter is now added drop by drop, and then the remainder of the silver solution in a similar

manner. Some of the silver salt is sure to be found crystallized on the edge and sides of the test-tube. This is re-dissolved, as before, in a little water and half an ounce of alcohol, and added with the same precautions. If the above details have been carefully carried out, the colour of a candle or gas-flame, when viewed through the liquid which runs down the inside of the glass jar after agitation, should appear of a deep orange approaching to a ruby tint. When in this condition, it may be judged that it has been rightly prepared. With the glass rod a drop or two of the emulsion should be dropped on to small strips of glass, and examined by daylight for structure, &c. When viewed through a window, the principal part of the light transmitted should be orange. A little potassium *chromate* should be dropped on to the emulsion on the plate, and a bright red colour will show that the silver is in excess, which is what is required in our case. If this colouration be absent, it will indicate that the soluble bromide is in excess, which, in some modifications of the same process, is what may be desired. The emulsion must next be decanted off into a bottle capable of containing at least double the amount of fluid—that is, at least 20 ounces—and it should then be shaken for ten minutes. It may now be put on one side for from sixteen to twenty-four hours, when it will be ready for the next operation.

We will now give a slightly different method for mixing the silver and the soluble bromide, which has been adopted by some people, amongst others by Warnerke, to whom the writer is much indebted for information on various points.

A couple of corks, D and E (fig. 2), which should fit the necks of the bottles A and B, are bored with holes just

wide enough to admit a glass tube, C, which has a diameter of bore of about one-eighth of an inch. The whole of the bromide is dissolved in half the amount of collodion used,

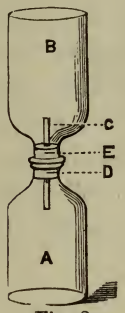


Fig. 2.

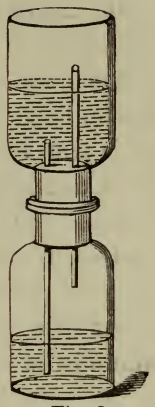


Fig. 3.

and placed in the bottle A, which (like B) should have sufficient capacity to hold double the amount of emulsion to be made up; the cork D, with the glass rod C, should next be fitted into it. Into the other bottle, B, the silver nitrate solution is added to the collodion, sufficient alcohol and water being used to keep it in thorough solution. The bored cork, E, is then fitted into the neck, and the far end of the glass tube deftly inserted, and the tops of the bottles brought close together. The hands then grasp the necks, and the contents are shaken up, when a little of B gradually finds its way into A. The positions of the bottles are then reversed, and a little of the contents of A shaken into B; when each of the bottles seems to contain emulsion equally dense, the whole of one bottle is gradually caused to drop into the other, and by this means a perfect emulsion is obtained. The emulsion may be made even more

rapidly by adopting the contrivance shown in Fig. 3, in which there are two tubes, one always acting as an inlet for air, whilst through the other the collodion finds a passage. In this case, narrow bored tubes are advisable, certainly not greater than one-eighth of an inch.

Now it has been said that in sixteen to twenty-four hours the emulsion will be ready for pouring out. This statement is true for the particular emulsion described, but it is not necessarily true for emulsions when other soluble bromides are employed. Thus we find that Col. Wortley stated to the Photographic Society of Great Britain, on 14th March, 1876, that the following is the time necessary for emulsions made with the following soluble bromides to match:—

Manganese	7½ hours
Cadmium	9 „
Strontium	10 „
Magnesium	10 „
Zinc	10½ „
Cerium	14 „
Potassium	14 „
Cinchonine	15 „
Sodium	15¼ „
Calcium...	17 „
Ammonium	17½ „
Uranium	17½ „
Barium	19 „

It will be noticed that Colonel Wortley gives zinc emulsion ten and a-half hours, as the time for attaining the maximum sensitiveness. The discrepancy is probably due to the greater viscosity of the collodion employed in

the one case as compared with the other. The list, however, is useful as showing the comparative times that should be allowed for ripening. We might here leave the emulsion as ready for coating plates after proper dilution, but we will further suppose that it is to be washed, a modification introduced by Bolton, one of the originators of the bromide emulsion process. The first step to be taken is to allow the solvents to evaporate.

Evaporating the Solvents.—An emulsion generally may be prepared in the afternoon of one day, well shaken before leaving the laboratory, and on the next day, about noon, the emulsion will be ready for drying. The mode adopted by the writer is as follows:—The emulsion is poured out into a flat dish, to a depth of a quarter of an inch, and placed in a dark room, the temperature of the latter being raised, if possible, to 70°. For the ten ounces of emulsion made, a porcelain dish, about 14 by 12 by three-quarters of an inch deep, is required.

After a short interval it will be found that a skin forms on the surface of the collodion; this is broken up with a glass rod, and a fresh liquid surface given to it. Every half hour the whole of the emulsion is thoroughly well stirred up, till it begins to break into lumps, when it can be left a short time, for the solvents still further to evaporate. It is ready for the first washing when the lumps require a little force to break them up—in other words, when they are about the same consistency as a collodion film before dipping into the bath. The mass is then removed to a glass beaker, and covered with distilled water. At this point we have a good test as to whether the evaporation of the solvents has been continued far enough. If only a few of the lumps rise to

the surface, the evaporation has been sufficient; if, on the other hand, the majority float on the surface of the water, it has not been continued long enough. The reason of this tendency of the lumps to rise to the surface is due to the light specific gravity of the ether and alcohol, which, even with the weight of the solid matter, is not sufficient to counterbalance the specific gravity of the water.

This method of eliminating the solvents is, however, wasteful, and, if preferred, resort may be had to a still such as already described (page 28); but this method should not be adopted *unless all acid be omitted* previous to distillation, since boiling an emulsion in its presence produces a very horny film. The acid must be applied in the first wash water. Let it be recollected that where the bromide is not in excess, *but where there is an excess of silver nitrate, nitric acid or its equivalent must be added to the emulsion itself, or to the first wash-water*—the time of addition being dependent on the circumstances already explained. *The whole of the operations up to the first washing may be carried on in the light.* The flask may be replaced by a wide-necked bottle of some couple of inches diameter, in the mouth of which a cork is fitted, carrying a bent tube. The thinner the bottle the better, since there is less liability for the bottle to break. The bottle attached to the Liebig's condenser should be placed in the water bath filled with cold water, and the gas or spirit lamp should not be lighted until everything is arranged. The water may now be gradually warmed, and when a temperature of 98° F. is reached, the ether will begin to evaporate, and condense into the bottle placed at the other end of the condenser. The temperature should be kept down till half the quantity of ether that is

supposed to be present has come over, after which the water may be allowed to boil, and the ether and spirit will come over together at a temperature of about 160°. When the thermometer rises to 173°, spirit alone is being distilled. The emulsion will continue fluid almost to the last drop; but when it is seen that the alcohol is only condensed drop by drop, the bottle should be removed and the contents placed in a dish to cool and solidify. This will take place in a very few minutes, and the pellicle will be in a pulverulent form, and readily amenable to washing. There is no danger attending this distillation if the water bath be used, but if the naked flame be applied a disaster is nearly sure to occur, since ether vapour, when mixed with air, forms an explosive compound; the corks closing the bottle or flask should therefore fit tightly. It must also be remembered that if a common bottle (such as described) be used, the water should be *cold* when it is immersed in it, and very gradually heated up, so that its contents may be of pretty nearly the same temperature as the external water. In M. Chardon's process, as subsequently given, it will be seen how this evaporation of the solvents, previous to washing, may be dispensed with. It is hardly worth while to repeat the method here, more particularly when, in some respects, the above is really superior to it; at least, so the writer has found.

For the above quantity of emulsion, 1 dr. of nitric acid, which will be ample to secure freedom from fog, should be dropped into the dish, and distilled water added. After a couple of hours the true washing may commence.

The emulsion may be placed in a jar or jam pot, and be covered with water where it can stand two or three

hours in the dark without detriment, when it should be changed. The way in which the washing can be economically effected, as regards time, is as follows:—A piece of coarse calico which has previously been washed in carbonate of soda, and then well rinsed, and dried, is spread over the top of a second glass jar or large jam pot, and the contents of the first thrown on to it. The calico acts as a strainer, and the solid pellicle is left on it. The calico is next taken up by the sides, and the contents are twisted up in it, and as much as possible of the liquid then wrung out. The calico is untwisted, and a bag formed by tying up the ends, to hold the emulsion, which is shaken up and immersed in fresh distilled water. After a quarter of an hour the wringing operations are again proceeded with, and this process repeated three or four times. The expelled water should now be tested for free silver nitrate by a drop of hydrochloric acid. If it gives more than a slight milkiness, such as is produced by adding silver nitrate to water containing a grain of common salt to the gallon, it must be washed till this maximum is attained.

Preparing the Pellicle for Re-emulsifying.—A very important part of emulsion making is now to be touched upon, viz., getting rid of the water held in the pellicular mass.

To commence with, as much water as possible should be squeezed out, and then we may proceed in one of these ways.

1st. We may lay it out flat on a piece of blotting-paper, and allow it to dry spontaneously. 2nd. We may put it in a flat porcelain dish, and place it in a water bath, the temperature of which can never exceed 212°, and thus all moisture may be got rid of. In this proceeding

the very greatest care is necessary, as the emulsion is apt to become very hard indeed, so much so as to be scarcely soluble; in addition to which, it is often apt to blacken spontaneously. The third method is one which we can confidently recommend for washed emulsion, being very simple, and absolutely improving its qualities when redissolved. This is simply to cover it with rectified spirit ·820 after as much water as possible has been squeezed out. In an hour's time the excess is drained off, and the pellicle is squeezed in the cotton rag as before. It is then once more covered with the spirit, and left for half an hour, when, after draining away the superfluous spirit, it is ready for re-emulsifying. If it be desired to keep the pellicle in a solid state, it will only be necessary to expose it to the air for a few hours, when it will be found quite dry.

It is instructive to examine the washings from the spirit. It will be found that there is a certain small quantity of silver bromide in suspension, which can be filtered out. If the spirit be distilled over, a semi-opaque liquid residue will be left, having a very high boiling point, a strong and very disagreeable smell, and containing some organic salt of silver, which discolours in the light. It may be said that this organic compound is necessary for density of image; but a trial of the emulsion washed in this way will prove the contrary; in addition to which, it will be found much freer from spots than that washed and dried by the first two methods indicated above.

There are some pyroxylines which it would be dangerous to treat in this manner, since they are soluble, to a certain extent, in absolute alcohol; but it seems to the writer that any such pyroxylines are detrimental when washed

collodio-bromide emulsion is in question. If they are employed, the old methods must be adopted.

The dried (or moist with alcohol) pellicle has next to be dissolved in its proper proportions of solvents, which are about 6 grains of pyroxyline to every ounce of the two when mixed. It is better to make it up first to the strength of 9 grains of pyroxyline, and then to add the remaining solvents, since the colour of the emulsion seems to be better when a greater degree of viscidity is present when the pellicle begins dissolving. In two or three hours the whole of the silver bromide should be in suspension. It will be found, however, that there is an improvement in the quality of the film after the lapse of a couple of days, or even more. A plate should be tried before diluting down the collodion with more ether and alcohol, in order to test its flowing qualities, and to note the opacity of the film.

In our own experience we like a film through which, when freshly coated, the light from a gas jet can be seen, but which, when dried, is perfectly opaque. In this condition the film is tough, requires no backing, and is always capable of giving sufficient density by alkaline development alone.

CHAPTER IV.

PREPARATION AND DEVELOPMENT OF THE PLATE.

It is not needful to give any minute particulars regarding the cleaning of the plate; though, perhaps, a few general remarks may be useful. In our own practice we usually soak the plates in nitric acid and water, and then wash under the tap, and carefully dry with a cloth; a cream of tripoli powder in alcohol is then rubbed over the plate, and allowed to dry. When a plate is required for use, the tripoli is rubbed off with a soft cloth, and it is left unpolished; a small piece of blotting-paper is then folded up in the shape of a small spill, and dipped in a solution of albumen in water (the strength is immaterial), and the plate is given an edging by placing the moistened end of the spill beneath the thumb of the right hand, and drawing it round the edge of the plate. By this means a "safe edge" is given to it. The amount of fluid required is so small that the first edge may be dry before the last is finished, and yet sufficient for the purpose will be on the plate.

Some persons rub French chalk or talc over the surface of the plate, and this will be found effective when using washed emulsion, without giving an edging; but we

honestly confess that where a preservative is used, this is hardly sufficient. In our own experience a film will adhere to the surface when it is only *once* wetted with water, but not twice. In this case a substratum must be employed to cause the necessary adhesion of the film to the plate. For the substratum nothing is better than gelatine made as follows:—

Sheet gelatine ...	...	...	75 grains
Distilled water ...	...	...	60 ounces
Ammonia ...	...	...	¼ ounce

The gelatine should be first softened in half the quantity of water, and the remainder added in the boiling state, which will dissolve it; when cool the ammonia should be added.

Mr. Henry Cooper has introduced a new gelatine substratum, the preparation and application of which he describes as follows. After stating that though other experiments may modify them, the proportions given answer well, and do not injure the sensitiveness of the films:—

"Soak sixty grains of Nelson's photographic gelatine in water, drain, and pour on enough boiling water to make eight fluid ounces. Now add two drachms of a ten-grain solution of chrome alum, and stir vigorously for a minute or two. Filter the solution through paper into a clean measure, keeping it warm and avoiding air-bubbles.

"To save trouble, a large quantity of each of the solutions, the gelatine and the chrome alum, may be prepared, and will keep for a long time if a little pure carbolic acid be added to each. No more must be *mixed* than is required for the batch of plates, as when the compound solution has once become cold, it cannot be again liquefied

with heat. The measure and filter used must be well washed with warm water as soon as done with, for the same reason."

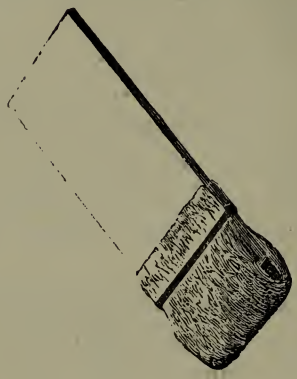
Albumen may also be used.

White of egg	...	...	...	1 ounce
Water	...	...	...	... 100 ounces
Ammonia ...	...	...	...	5 drops

50 grains of dried albumen may be substituted for the white of egg. The albumen and water should be well shaken together in a bottle for five minutes, and then be filtered through fine filter paper, taking care to avoid all air-bubbles.

The cleaning of the plate is of much greater importance where a substratum is used, than where it is omitted, the great difficulty being to get an even film on the surface. It is impossible to get this if there be the least repellent action between it and water. What the writer recommends is, that the plates be soaked in nitric acid, and be well rubbed with it by means of a pad of cotton wool *(freed from all resinous matter by previous soaking in a strong alkaline carbonate, and then thoroughly washed and dried)*, and that when this is washed away under the tap, that it be followed by a solution of potash, alcohol, and water, also rubbed in with a pad of wool. When water flows evenly over the surface, the plate should be rinsed in distilled water, and, after a short draining, the gelatine or albumen solution should be flowed over it, and drained off immediately. A very thin substratum will thus be given, which will dry rapidly, and be adherent to every part of the surface. Another plan is to use the Blanchard brush. A brush is made of swan's-down calico, as follows:—A strip of glass, about six

inches long by two broad, should be procured, and round one end should be attached, by thread or india-rubber band, a double fold of swan's-down calico. This brush



should be dipped in the albumen, and the excess squeezed out against the beaker. The plate should then be brushed smoothly down the surface in parallel lines to within one-eighth of an inch of its edges, set up to dry on blotting-paper, and protected from dust. When dried (which it should be spontaneously), the plate will be ready for the collodion.

Some photographers recommend the use of india-rubber for the substratum.

India-rubber	...	...	...	1 grain
Chloroform	...	...	...	

Or,

Benzole	...	...	...	1 ounce

Unless this be very clear, and free from all residue, a negative taken on a plate so coated is apt to show markings. There are, however, some emulsions which seem

to be totally independent of the character of a substratum, and will not show these markings, even when the india-rubber solution is not bright.

Coating the Plate.—When plates are to be coated the emulsion should be well shaken for three or four minutes, and be then allowed to subside for ten minutes. The top portion should then be filtered through washed cotton-wool (see page 45) into a clean and dry bottle. The cotton-wool should be placed in the neck of a funnel, and be not too tightly pressed down; and a little strong alcohol passed through it to moisten it. The first lot of emulsion passing through the funnel should be returned to the bottle, and filtered again. The amount of emulsion required varies with the number and size of the plates used; about ten ounces will usually coat ten plates. The filtered emulsion is poured over the plate in the usual manner, and the plate tilted up, and rocked to and fro till the ridges and furrows, so often visible in these plates, have disappeared. The surplus collodion should be returned through the filter into another bottle, as by so doing a fresh portion of the emulsion is used for each plate coated, and there will be a consequent freedom from specks due to any dust which may have fallen on a plate previously coated. If this be a washed emulsion, it should now be dried. In one's own dark room there is nothing so convenient as a hot air bath, such as used by chemists in their laboratory. They can be obtained up to a size which will take $8\frac{1}{2}$ by $6\frac{1}{2}$ plates. It is a good precaution to line the inside with varnished paper, to prevent the remote chance of any metallic specks depositing on the plate during drying.* If

* For details of a drying cupboard see "Instruction in Photography," 3rd edition (Piper and Carter), page 58.

this be not at hand, the small piece of apparatus recommended by Woodbury is very effective. It consists of an iron tripod stand, such as used in the laboratories, a flat sheet of cast iron,* and a spirit lamp when gas is not available. The iron plate is placed on the iron tripod, and the spirit lamp beneath it. It is advisable to place a couple of pieces of blotting-paper beneath the plate which is to be dried. By using the blotting-paper the plate will be dried and heated uniformly throughout, which is not the case when it is placed directly on the cast iron plate, for curvature in either will prevent the two surfaces coming in contact. The heat should be so great that to touch the surface of the blotting-paper is unpleasant to the fingers, and the glass should be allowed to assume the same temperature. It may be laid down as a maxim that the more rapid the drying, the greater freedom there will be from all spots.

Where a preservative is to be employed with a *washed emulsion*, the plate must be washed with water till all greasiness disappears, when it may be applied at once. If an unwashed emulsion be used, the plate must be well washed in distilled water, till all excess of haloid salt, if that be in excess—or, *as a rule*, of the silver nitrate, if that be in excess—be thoroughly eliminated. The preservative may then be applied by flooding the film with it, or by immersing the plate in a flat dish or dipping bath containing it. The plates are in this case usually allowed to dry spontaneously, but they are generally improved by a final dry over the iron plate as directed above.

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* An old pikelet iron, in one instance we are aware of, has been successfully employed.

In subsequent pages will be found a description of preservatives which may be applied to washed emulsion with success.

Backing the Plate.—With some kinds of emulsion, more particularly if a gum or albumen preservative be used, the films are very transparent, and the image is subject to the well-known blurring due to light scattered by the particles of the sensitive compound, and reflected from the back of the plate. This defect is in a measure cured by applying some non-actinic varnish to the back of the plate. This backing may be made as follows :—

Powdered burnt sienna	1 ounce
Gum	1 „
Glycerine	2 drachms
Water	10 ounces

The solution can be brushed on with a hog's bristle brush. Ordinary printers' paper coated with gum arabic, stained with aurine or a blue absorbent dye, and fastened on the plate, is as clean a method of backing a plate as can be desired. Whichever backing is employed, it should be removed previous to the development of the plate, and it is often convenient to do so after the alcohol has been applied to the surface of the film, and before washing with water. The alcohol repels any water containing the soluble part of the backing, and thus prevants staining of the image. A small tuft of cotton wool will remove the backing given above.

The exposure necessary for the washed emulsion already described is very constant; with a lens of aperture $\frac{f}{20}$, and in a fair light, thirty seconds will be found to be ample when using the alkaline or ferrous oxalate developer.

Developing the Plate.—For emulsion work, an alkaline (or kindred) developer of some kind is almost an essential, for though faint detail can be developed by pyrogallic acid alone, in *most* cases such a procedure entails a prolonged exposure.

The following are formulæ for the alkaline developer which the writer can recommend, having been in use by him for several years past:

(1).—Pyrogallic acid...	6 grains
Water	1 ounce
(2).—Potassium bromide	20 grains
Water	1 ounce
(3).—Ammonia	1 part
Water	32 parts

The developer given by Col. Wortley is as follows:—

(*a*).—Pyrogallic acid...	96 grains
Methylated alcohol	1 ounce
(*b*).—Potassium bromide	12 grains
Water distilled...	1 ounce
(*c*).—Ammonium carbonate	30 grains
Water	1 ounce

Or,

Liquor ammonia	25 minims
Water	1 ounce

To develop a washed emulsion plate having no preservative: by the first formula one part of (1), two parts of (2), and one part of (3) are taken and well mixed in the developing cup; by the last formula, one part of (*a*), two of (*b*), and four of (*c*), are taken and mixed.

The next developer, and that one which seemingly

will become a general favourite, is the ferrous oxalate developer, just formally introduced by Mr. W. Willis, Jun., though Mr. Carey Lea pointed out previously that it could be used. To prepare the developer make up

Ferrous sulphate ... ... A saturated solution

Next add to it sufficient oxalic acid (a saturated solution) to cause all the iron to be precipitated as ferrous oxalate, which is of a bright lemon colour, and very heavy, sinking rapidly to the bottom of the vessel.

The ferrous oxalate must, of course, be washed, and, since it is heavy, this can be readily accomplished by the method of decantation. The supernatant fluid is carefully poured off, and the vessel is then filled with fresh water (tap water will answer), which, after well stirring, is poured off, and the vessel filled up again. This washing may be considered to be complete after six changes of water.

A saturated solution of the neutral potassium oxalate is next required, and this can be prepared by adding a saturated solution of caustic potash to a saturated solution of oxalic acid, till a very faint blue colouration is given to red litmus paper. A crystal of oxalic acid is then added, and the neutral solution will be formed.

The ferrous oxalate is next thrown into the warm potassium oxalate solution; only so much of the oxalate being added as to leave a slight portion of the ferrous compound undissolved. The solution will be of a deep red colour, and, when cold, should be filtered free of all deposit. It is then ready for use. In our own experience, it is better to add a grain, or even three grains, of potassium bromide to it immediately before use, since,

unrestrained, it has an undoubted tendency to fog the picture. If this addition be made, the negative will develop bright and clean.

Where proper exposure has been given, it may be used of full strength; but where over-exposure is suspected, it should be of only three-quarter strength; that is, to each three drachms of it one drachm of water should be added.

The exposure required for this developer seems to be about two-thirds of that required for the alkaline developer given above, and is, therefore, a decided gain to the photographer.

There is a great charm in this developer, the plates gaining intensity steadily, and without any tendency of being overdone, and the negatives give brilliant prints.

The ferrous oxalate becomes oxidized if it be left in contact with the air. It is, therefore, perhaps inadvisable to make up more of it than is necessary for two or three days' supply. Mr. Swan, however, states that a bundle of bright iron wire kept in the solution will prevent its losing its developing power; and Mr. Woodbury recommends the addition of a pinch of fresh ferrous oxalate, when in the inactive state, to restore it. On the whole, we recommend the solution to be made up merely as required, since it can be speedily prepared by keeping in stock saturated solutions of potassium oxalate and of oxalic acid.

We will now imagine that the plate has been exposed, and that we are to develop the image. After taking the plate out of the slide it is carefully dusted, and a solution of equal parts of alcohol and water is flowed over it to soften the film. It is then either washed under the tap, if the water supply be of good quality, or is

immersed in a dish of rain water previously filtered through charcoal. When all repellent action between the spirit and water is obliterated, the mixed proportions of solutions indicated above are carefully flowed over the plate, and almost immediately poured back. The image ought to appear gradually and without veil. If it shows unwillingness to appear, a fresh solution should be made, omitting half the bromide, and this will probably be effective. Should there not be sufficient density, resort must be had to the ordinary acid intensifier.

(1).—Pyrogallic acid...	...	...	2 grains
Citric acid	...	...	...	2 „
Water ...	...	...	...	1 ounce

And,

(2).—Silver nitrate	...	...	...	20 grains
Water ...	...	...	...	1 ounce

The plate must be well washed before using this. Sufficient of No. 1 to cover this plate should be flowed over it, and four or five drops of No. 2 dropped into the cup, and the solution from off the plate returned on to it. The intensification should then proceed in the ordinary manner.

There is another developer, introduced originally by M. Sammann, of Paris, which is popularly called the "hydrosulphite developer." It has not been much employed, owing to the trouble there is in making it. It is, however, very effective; and Mr. Berkeley, an advanced emulsion worker, recommends it strongly.

We give M. Sammann's last directions. Make the following stock solutions :—

(1.) Pyrogallic acid ... ... 1 ounce
Saturated solution of salycic acid in water ... ... 20 ounces

(2.) Sodium bisulphite ... ... 1 ounce
Sodium sulphite... ... ... 80 grains
Water ... ... 4 ounces

20 grains of sodium borate may be substituted for the sodium sulphite.

When it is required to make the sodium hydrosulphite, a vial is half filled with granulated zinc, and enough of this solution is poured in to fill up the interstices. After half-an-hour the reaction is complete. The solution is poured off into a stoppered bottle, where it will keep, but only for a few hours.

The zinc and vial must be well washed, in order to be ready for the next quantity which may be required. M. Sammann says that the bisulphite must be quite free from sulphurous acid, which, if present, must be neutralized by sodium carbonate. One part of it should dissolve in two of water at the ordinary temperature.

Before development, the plates are flooded with a solution of—

Tannin ... ... 10 grains
Water ... ... 1 ounce

They are then washed and drained. One part of No. 1 and four parts of No. 2 are then mixed together, and placed in a dish containing the plate, which it is just big enough to hold. When all the detail is well out, it is probable that the negative will have sufficient printing density, as the development is very slow and gradual. If the pyroxyline be of too "organic" a character, a

white veil is sometimes seen on the shadows, which, however, disappears on varnishing. The intensity may be given in the usual manner by pyrogallic acid and silver, according to the formula given above, if it be lacking. Mr. Berkeley states that this developer may be made alkaline with ammonia, in which case the sodium sulphite may be omitted.

Some prefer to develop their plates in a dish; indeed, for the last developer a dish is almost a necessity, and for gelatino-emulsion plates it is highly desirable. The following description will show how a cheap one may be constructed. Suppose the size of the plate to be 7 by 5 inches. An ordinary 9 by 7 plate is taken, and on it are cemented four strips of quarter-inch thick glass as shown in the figure. The cement used may be marine

glue, which, with every part of the glass, is heated, in order to give perfect adhesion. The position of the plate is shown by the dotted line in the figure. Sufficient developer to cover the whole of the plate must be employed, in order that the dish may be of any use.

The colour of the negatives produced by the above three developers varies very much. By the alkaline method we may have a tint of deposit from olive green to brick

red; a great deal, seemingly, depends on the fineness of the original silver bromide. The finer it is the redder will be the film, whilst a black deposit is probably coarser than any other. A deposit which is bluish when viewed by transmitted light is probably intermediate between the two, and olive green tint again lying between the reddish and the blue.

The ferrous oxalate developer gives a blue black deposit, as a rule, and is coarser than that given by the alkaline or hydrosulphite developer. The rapidity of development must also influence the colour, since, whatever method be adopted, the metallic silver is deposited, as well as reduced, more particularly in the alkaline method.

To develop a plate having a preservative, a little thought should be taken as to the nature of the latter, as already pointed out at page 18. It is evidently useless to waste alcohol if it is not soluble in it. In cases where it is insoluble the preliminary flooding with the spirit should be omitted, and the soluble matter entirely removed by water. Since the object of the alcohol was to open the pores of the collodion, evidently the same will be accomplished by removing the soluble matter which filled them up.

A negative that is fully developed by any of these methods should show reduced silver bromide next to the glass plate in the most opaque parts; so complete should this be, that if the image be dissolved away by nitric acid, we should have a positive picture left behind formed of unaltered bromide, and perfect in gradation.

The negative should be fixed with potassium cyanide or sodium hyposulphite.

Potassium cyanide	25 grains
Water	1 ounce

Or

Sodium hyposulphite	1 ounce
Water	6 ounces

A dipping bath for the latter will be found advantageous for studio work. There are some images which will not stand the cyanide; it may be because the metallic silver is in a very fine state of division. This seems all the more probable since we know that in this state it is attacked by the cyanide.

The Light Admissible for Preparing and Developing Plates.—The quantity and kind of light that may be allowed in preparing and developing plates is a rather difficult subject on which to treat. With some emulsions, daylight of any kind admitted through any kind of glass is quite inadmissible, be the glass orange or ruby, as some emulsions are decidedly sensitive to the red rays. The writer himself prefers to develop and prepare plates by candle-light, for, however sensitive a plate may be, he has found none which is affected in half-a-minute by a gas-light shielded by orange paper, if placed six feet off. This can be well understood when it is considered that if a plate be exposed behind a negative to the naked flame of an ordinary gas jet, at a distance of one foot, a properly exposed transparency cannot be obtained in less than half of a second; at six feet off this would take thirty-six times that, or about ten seconds. Now no plate now made is as sensitive to the orange as to the blue by at least twenty times. This would give two hundred seconds, or more than three minutes, for a plate which

is the most sensitive to the orange rays to be fully exposed.

When a plate is developed, the flowing with alcohol and the washing with water may be carried out in almost absolute darkness, and it is only necessary to approach the light when the actual developer is to be flowed on. The image should appear in less than fifteen seconds, and after it has been commenced there is very little danger of fog, as the silver bromide becomes, as it were, almost inert under the influence of the developer; at all events, it loses very much of its sensitiveness.

In any case, for emulsion work, the windows of the dark room should be glazed with ruby glass in preference to any other, as an emulsion is, as a rule, insensitive to the rays passing through such a medium, provided direct sunlight be not admitted. If the sun at any time strike on the window, it should be shaded by an outside blind of yellow calico. For covering the globe of a gas or oil lamp, there is nothing better than varnish mixed with two kinds of dyes. To one aurine may be added, and to the other aniline scarlet. The inside of the globe may be coated with one, and the outside with the other varnish; the light penetrating the two will be deprived of most of the rays which act chemically on silver bromide.

For developing plates away from home, we have found that a useful piece of apparatus can be easily made. Take a sheet of cardboard of the size of about 2 feet by 1 foot 6 inches. Lay off from the 2 feet side distances of 6 inches from each corner, and with a penknife cut half through the card in a line parallel to the ends. These will form flaps, which can be folded over to meet in the centre. From the centre portion, and 6 inches from the

bottom, mark out a square of 8 inches; cut round three of the sides, but only half cut through the bottom side, the penknife being applied from the inside of screen. This will allow a square flap to fold downwards towards the outside. On the inside of the opening may be pasted or hung two or or three folds of orange paper; or a sheet of gelatine (made by preparing a skin on a glass plate, as for heliotypy, and dyeing it deeply with aurine or aniline scarlet) may be glued to it. The candle is placed behind the screen, which should stand, supported by the two wings, in front of the operator. When packed for travelling the flaps are folded up, and it can be placed in the portmanteau with the greatest facility.

CHAPTER V.

CAREY LEA'S CHLORO-BROMIDE EMULSION.

In the year 1869, Mr. Carey Lea, the able American photographer and experimentalist, brought forward what is known as the chloro-bromide process, in which the new feature of the introduction of a chloride into a bromide is announced, by *preference using cupric chloride.*

The excess of silver employed by Mr. Lea in this process was very little over that required for the full saturation of the bromide and chloride, and after keeping beyond a certain time, in the writer's experience fog was always present when this formula was followed. Mr. Lea himself seems to have found this, for in March of 1870 he introduced a modification of the process, which enabled any amount of excess of silver nitrate to be used, without any danger of fog being produced in development. By this modification the theoretical considerations already pointed out were fulfilled. As the process is still one of the best, we prefer to give it in the author's own words, as extracted from the *Philadelphia Photographer.*

"In the introduction of a chloride into the collodion I found a material gain. Since I wrote the paper in which

I described that innovation, and which was published a few months ago, I have carried on an uninterrupted series of experiments. At last I have reached the secret of the whole difficulty, and have found its complete cure. To make the collodio-bromide process work with regular success, it is necessary to add an acid, preferably a strong mineral acid, to the collodion.

"This may seem at first an extraordinary proposition, but upon examination it will be found right, theoretically as well as practically. In the wet process we have often acid in every stage of the work. The collodion is acid, or, at least, contains free iodine, which is virtually the same thing; the bath is generally acidified; and the development is usually acid also. Now it is well known that bromide of silver bears acid very much better than iodide; that is to say, that the introduction of a bromide into the ordinary collodion for the wet process enables the bath to be acidulated without loss of sensitiveness, which was not the case when simply iodized collodions were used. With the total exclusion of iodide of silver, of course the capacity to bear acid is increased. And yet we have committed the absurdity of trying to work the collodio-bromide process with purely neutral materials, thus making it a solitary exception in the whole range of collodion methods. Even in the bromide process with a bath, acid is used, and very liberally; in fact, more so than in any other process, wet or dry.

"The negatives afforded by the acidified collodio-bromide process are remarkably beautiful in appearance. They are beautifully clean, show the details even in the high lights, when viewed as positives by reflected light, held before a dark background. Very deep shadow, such

as an open window, is represented by clean glass. The high lights when the plate is looked at by reflected daylight have a peculiar metallized coppery look. The back of the film as seen through the glass is just as clean and brilliant as the front.

"The acid which I use in preference is *aqua regia* in its active state. It is only necessary to mix in a stoppered vial an ounce of ordinary nitric acid and two ounces of ordinary hydrochloric acid, and to gently warm the bottle until the acids react upon each other, and the mixture passes into its active state by formation of chloronitrous acid. This is indicated by the liquid becoming orange colour, and by the formation of small bubbles of gas in it. The stopper is then put in, and the bottle set aside for use. A convenient way to apply the heat is simply to set the vial on a stove. The proper proportion is one to two drops to the ounce of collodion. A considerable amount of experience will be necessary to decide which is best; at present I incline to one drop to the ounce, but have at times used two very satisfactorily. The best way to apply the acid is to drop it into a very small porcelain capsule, and then turn into the collodion bottle as much as will run off. To get the rest in, pour a drachm or two of the collodion into the capsule, and back again; at first there will be a gelatinous drop formed, but by repeating the pouring six or eight times this will re-dissolve, and the whole of the acid be transferred. The time of acidifying seems not to be very important; I have sometimes added the acid immediately before sensitizing, and sometimes a month before; in both cases with good results.

"The effect of the acidifying is extremely marked. The

excess of nitrate of silver, which before could not be brought into actual solution without fogging, has no longer any such tendency. This I have tested critically by dissolving the whole of the nitrate of silver beforehand, and then keeping the materials for a day, or even two days, in contact, with frequent shaking. Even with this treatment the negatives came out perfectly clear and bright, without the use of bromide in the development. Indeed, it is doubtful if that agent will ever be necessary; at least, so far in my numerous experimental plates I have never employed it.

"It seems proper here to guard against a very obvious mistake, which, nevertheless, occurred on a previous occasion. I do not suppose that the use of acid would be of the slightest benefit to those who work the collodio-bromide process with excess of bromide, nor was the chloride of copper intended to be so used."

The supposition made by Mr. Lea in this concluding paragraph we know is perfectly correct, for if we add any mineral acid, nitric or other, to the bromide, we do not secure more immunity from fog than if it is omitted altogether, and the introduction of the chloride is simply useless, as it cannot displace any bromide.

"The following are the manipulations:—

"*Collodion.*

Ether	...	20 fl. ounces
Alcohol	...	12 „
Intense pyroxyline ...	...	162 grains
Bromide of cadmium ...	...	320 „
„ ammonium	...	64 „

Add half the alcohol to all the ether, and shake up with

the pyroxyline; throw the salts into a flask with the rest of the alcohol, and heat till dissolved; add to the other portion, shake up well, and place in a warm, light place for three weeks; it will be better still in two or three months.

"This collodion will require sixteen grains to the ounce of nitrate of silver to sensitize it. I prefer, and always use, fused nitrate, and recommend it for all collodio-bromide work, as much preferable to the crystallized.

"Having measured out the quantity of collodion to be sensitized, weigh out sixteen grains of very finely powdered nitrate of silver to each ounce, throw it into a test-tube or flask, and pour over it alcohol of 95 per cent. in the proportion of one drachm to each eight grains of nitrate; boil for a few minutes, and the nitrate will dissolve; pour it now in successive portions into the collodion, shaking up well after each; shake about five minutes after the last portion is added, and every few times thereafter; use twenty-four hours after sensitizing.

"I have, at various times during the past years, used this method of introducing the whole of the nitrate in actual solution. In the collodio-bromide process, as originally described by Messrs. Sayce and Bolton, it is not appropriate, because in that process the whole of the silver must not be in actual solution. But in this present acidified process it is desirable to have the silver altogether in solution; in fact, this point makes an extremely wide difference between this process and any other that has been hitherto described.

"In twenty or twenty-four hours after sensitizing the mixture will be in condition to use. The difference of a few hours will not be important, but it is best

not to exceed twenty-four. If kept too long there will be a disposition to fog in the shadows, and a want of brilliancy in the whole picture. The high lights, also, will not have their details well marked. The filtering is best done by putting a piece of soft, clean sponge in the neck of a funnel, and cutting a small circular filter of close-woven linen. The linen used for making these filters should be boiled for an hour with very weak caustic potash or soda, then well washed in hot water (of course without soap), and dried. This plan of filtering will be found excellent for all sorts of photographic collodions. Before filtering, the collodio-bromide mixture should rest quiet for two or three hours after its last shaking.

"For the preservative bath I recommend exclusively the two following, either of which gives good results.

"*Litmus Preservative.*

"Cover a quarter of a pound of good litmus with hot water; set a basin or plate over the bowl, and put in a warm place for a day; throw the paste upon a filter, and pour on hot water till the filtrate amounts to a quart (the filtration is slow); add a drachm of carbolic acid, and the litmus solution keeps good indefinitely.

Litmus solution...	1 ounce
Water	6 ounces
Gum-arabic	90 grains
Sugar (fine white)	90 „
Acetic acid (No. 8, or Beaufoy's)	25 minims

"The above quantity makes a convenient bath for a 6½ by 8½ plate.

"Throw the collodio-bromized plate into a pan of water

until the greasy marks are gone, and then pass it into this bath, where it will remain, with occasional agitation, about ten minutes. The time is not important; five minutes will be sufficient; fifteen will do no harm.

"*Tannin Preservative.*

"I have lately got good results with tannin by reducing the proportion greatly below what is ordinarily recommended. By so reducing it, I retain the beautiful variety of half-tint which is characteristic of gum, and which is greatly injured by using the ordinary quantity of tannin. I take—

Water	7½ ounces
Gum-arabic	90 grains
Sugar	90 „
Tannin	15 „

"The tannin is here used two grains to the ounce. The washing of the plate is the same as above.

"The litmus gives the softest and most sensitive plates, but needs an intenser cotton. The latter of the two preservatives will work well with a wider range of pyroxylines than the former, and give a brighter picture. The tannin is the easiest to succeed with, but the litmus, when well managed, undoubtedly gives the best negatives. In either case, the negatives are very beautiful; better looking or better printing negatives cannot be got with the wet process.

"*Development.*

"Prepare a sixty-grain alcoholic solution of pyrogallic acid and a forty-grain solution of ordinary carbonate of ammonia in water.

"To five ounces of water add half a drachm of the pyrogallic solution and a drachm of the carbonate ammonia. Agitate the pan to mix them well, raise one end, and put in the plate in the ordinary way. No washing or application of alcohol is needed. When the image is pretty well out, but thin, add another drachm of the ammonia solution, and density will quickly come.

"Bromide of potassium in the developer I have so far found wholly unnecessary. Nor will a re-development with silver be necessary, unless, perhaps, when some great mistake has been made in the exposure, which, with a good light, will be the same as for the wet process; but where the light is poor, or the contrasts great, the exposure will need to be prolonged.

"The above directions will probably be found sufficient for working the process. I am still endeavouring to improve it, if possible. I judge that the method of keeping the residues over, which I have always found useful in the other modification of collodio-bromide, in order to obtain dense opaque films, will be also valuable here, but have not as yet sufficiently tried it. I am also about to examine the applicability of hydrobromic acid with or without nitric acid, to the collodion, instead of hydrochloric. I scarcely expect, however, that it will prove advantageous, as the introduction of chloride of silver into the sensitive film is a decided advantage, as I have already proved in the case of chloride of copper. The aqua-regia here recommended may be used either as a substitute for the chloride of copper before proposed by me, or in conjunction with it. Either way has given me excellent results.

"In conclusion, I may say that I have never found

any photographic process so pleasant to work as this. The tedious washings after coating the plate, which consume so much time in some other processes, are here done away with; the plates are made easily, rapidly, and with great regularity. The two conditions of success are, to use a very intense cotton, and, at the same time, one which will make a very easy flowing collodion, for want of which latter quality mottled skies may result. The plates should be fixed in very weak hyposulphite, never in cyanide."

When this article was penned, the strong alkaline developer was unknown, and the development of these plates may be effected by the solutions given at page 50. In the process described, we have the first really workable collodio-bromide emulsion in which an excess of silver was used.

CHAPTER VI.

URANIUM DRY PLATES.

In June, 1871, Col. Wortley read a paper before the Photographic Society in which he stated that he had adopted Carey Lea's process, adding a greater quantity of silver nitrate in proportion to bromide than recommended by the latter gentleman. It is the following process, however, which is novel in its arrangement, by which Colonel Wortley is best known; and we do not hesitate to publish the form in which he originally gave the process to the public at a meeting of the (now defunct) Photographic Dry Plate Club.

The plain collodion is made with pyroxyline prepared at a high temperature.

The emulsion is made as follows:—

Plain collodion	1 ounce
Anhydrous cadmium bromide ...	7 grains
Uranium nitrate	30 „
Silver nitrate	13 „

The uranium nitrate should be pure, and *very slightly* acidified with nitric acid. The uranium salt and cadmium bromide should be dissolved in the collodion, and the nitrate of silver added as directed before. The plate should have a substratum, and be coated as usual; when

set, it is washed in distilled water till all greasiness disappears, when any of the usual preservatives may be flowed over it. Preservatives containing sufficient gum to give a protection to the film tend to cause blisters on development. Col. Wortley recommends the following as giving freedom from this annoyance.

The following stock solutions are prepared :—

No. 1. Salicine, enough to make a saturated solution in distilled water.

No. 2.	Tannin	... 60 grains
	Distilled water ...	... 1 ounce
No. 3.	Gallic acid ...	... 48 grains
	Alcohol	... 1 ounce

To make the preservative, take of—

No. 1.	... 2 ounces
No. 2.	... 1 ounce
No. 3.	... ½ „
Sugar	... 40 grains
Water	... 7 ounces

This preservative may be used over and over again with occasional filtering. The plates are best immersed in it.

Aurine may be introduced into the plain collodion, or else a backing must be given, to prevent blurring (p. 49).

The development of these plates may be carried out as given at page 50.

The *ordinary* pyrogallic acid intensifier may be employed with a thirty-grain solution of silver.

Either sodium hyposulphite or potassium cyanide may be used as fixing agents (see page 57). Intensification may be carried on after fixing if required. This, perhaps, is a safer plan than doing so before.

CHAPTER VII.

MR. HENRY COOPER'S PROCESSES.

We next give two processes, due to Mr. Henry Cooper, in which the silver salt is in defect instead of excess, and, as worked by that gentleman, they are everything that can be desired, though in our hands they have both proved slower than when an excess of silver was originally present.

The pyroxyline, prepared as given at page 24, may be used for the preparation of the collodion, or any good commercial sample will answer; but that prepared at a higher temperature than usual is recommended by Mr. Cooper. This gentleman's formula for the collodion stands as follows:—

Ether ·730	... 4 ounces
Alcohol ·805	... 2 „
Cadmium bromide ...	... 40 grains
Ammonium bromide ...	... 24 „
Pyroxyline	40 to 50 „

Twelve fluid drachms of this are measured into a four-ounce bottle. Having fused a sufficient quantity of silver nitrate for the purpose, and powdered it very

finely, weigh out 34½ grains, and place it in the bottom of a clean test-tube. Pour 3 drachms of alcohol, ·825, upon it, and raise it to the boiling point, shaking the silver in the alcohol occasionally. When cooled, pour off the dissolved silver nitrate from the undissolved nitrate into the collodion, little by little, shaking between each addition. Next add 3 drachms of alcohol to the undissolved portion, boil, let cool, and add as before. It will be found that the whole of the silver is dissolved, and the emulsion of silver bromide will be complete, though there will be an excess of 11½ grains of silver nitrate, 23 being sufficient for the 12 drachms; 12 drachms of the plain bromized collodion are next added, and here the bromide is in excess. In this condition the collodion can be kept for any length of time. When required for use, 11½ grains of silver, dissolved in 2 drachms of alcohol, are added in the method described above. After standing about an hour, the collodion is fit for use. If requisite, it may be filtered through tow or cotton-wool which has been treated as given at page 45. The last addition of the silver, therefore, leaves the bromide in *slight* excess, which is desirable for clean working.

If collodio-bromide be fully sensitized with silver, it is found that in three or four days' time it loses its sensitiveness. This may be avoided by adding each time, after preparing plates, a certain quantity of the bromized collodion to the residue, and re-sensitizing it, as before, when required.

If the collodion be horny, the alcohol containing the silver nitrate may be added boiling.

The plate is coated in non-actinic light, in the ordinary manner. When the film has set properly, immerse the

plate in pure water until the greasiness has disappeared. Withdraw it from the dish, and then immerse in a solution made as follows :—

(*Mr. Cooper's Preservative.*)

Gum-arabic	...	...	...	15 grains
Tannin ...	...	...	...	4 „
White sugar	...	...	...	4 „
Distilled water	...	...	...	1 ounce

Or,

(*The Liverpool Dry-Plate Company's Preservative.*)

Tannin ...	...	...	...	15 grains
Alcohol ...	...	...	...	15 minims
Water ...	...	...	...	1 ounce

The same preservative, containing salicine, as used in Col. Stuart Wortley's process, is also applicable.

These plates require a backing; the same as given at page 49 may be given. To avoid the backing, Mr. Cooper has suggested the use of aurine* in the collodion to prevent blurring. He makes a solution of 1 drachm of aurine to 1 ounce of alcohol. All impurities are precipitated, and about 30 drops of the solution are added to each ounce of collodion. With alkaline development, if not previously dissolved out, the colour is apt to change to a deep red. This is got rid of by washing with an alkali (liquor-ammonia answers well) or spirits of wine after fixing.

Alkaline development is usually employed, and for this method it is necessary to have the following solutions ready :—

* The aurine, however, diminishes sensitiveness.

No. 1	Pyrogallic acid	3 grains
	Water...	1 ounce

(This will not keep long, but should be made when required.)

No. 2.	Ammonium carbonate ...	1½ drachms
	Water	1 ounce

Or,

No. 2.	Liquor ammonia	1 part
	Water	12 parts

No. 3.	Potassium bromide ...	1 grain
	Water	1 ounce

No. 4.	Silver nitrate	20 grains
	Citric acid	25 „
	Water	1 ounce

Nos. 2, 3, and 4 will keep indefinitely.

The film should be flooded with alcohol and water (equal parts of each being used), and worked over it for a couple of minutes, till the surface is softened. If aurine have been used, the alcohol dissolves it out, leaving the film free from colour. If there be "backing," it should be removed directly after flooding with the alcohol, and before the film is washed with water (see page 49). The film should then be well washed under the tap. If there be every reason to suppose that proper exposure has been given, make a developing mixture in the following proportion :—

No. 1	1 drachm
No. 2	1 drop
No. 3	1 „

Sufficient should be taken to well cover the plate. Nos. 2 and 3 should be first dropped into the developing cup,

and finally No. 1 is added. (The necessity of stirring is prevented by this procedure.) Flood this over the plate. The image, if everything be *en règle*, should appear quickly, and the developer should be worked over the plate till all detail appears by reflected light. When this happens, another drop of No. 2 to each drachm should be dropped into the measure, and the solution poured back on to it as before, and the intensification with the stronger ammoniacal solution proceeded with. The intensity will gradually be increased, and it may happen that the requisite density will be obtained. Should the density not be sufficient, one drop of No. 4, with a drachm of No. 1, may be mixed, and intensification takes place in the ordinary manner. In the writer's experience, the colour and printing qualities of all negatives by this process are improved by even a slight application of the intensifier. This opinion coincides with that of Mr. Cooper.

Should the negative flash out at once on the application of the first developer, it is a sign of over-exposure of the plate. The developer should immediately be returned to the cup and the plate washed. Two drops extra of No. 3 must be added to the developer, and the development proceeded with as before. The potassium bromide keeps the shadows bright, and acts as a retarder; so much has it the latter qualification, that if a large quantity be added, the plate will refuse to develop at all. It is better to fix an over-exposed picture immediately the detail is all out, and intensify with pyrogallic acid and silver afterwards.

If traces of the picture refuse to appear after an application of the primary developer in three or four seconds, a fresh developer should be made up similar to the above, *omitting* the bromide of potassium. The picture will

probably appear satisfactorily when this course is adopted. When the detail is well out, the intensification should be carried on as given above.

The negative should be fixed with weak cyanide or sodium hyposulphite (see page 57).

MR. HENRY COOPER'S COLLODIO-BROMIDE PROCESS WITH A LACTATE.*

Mr. Cooper has modified the above general formula to attain a greater amount of sensitiveness. The pyroxyline used is made at a high temperature, and can be obtained from most photographic chemists. The collodion is made as follows:—

Anhydrous cadmium bromide ...	52 grains
Anhydrous calcium chloride ...	8 „
Pyroxyline	about 45 „
Ether, refined	4½ ounces
Alcohol	2½ „

To form the emulsion, take fourteen grains of powdered fused silver nitrate, and place it in a tiny glass flask. Pour upon it seven minims of distilled water, and dissolve by heat. Now pour in gently three drachms of absolute alcohol, and again warm over the spirit lamp until all the nitrate is taken up. Whilst the solution is still warm, add it gradually to seven drachms of the bromo-chlorized collodion, previously measured into a clean and dry stoppered bottle. The only precaution to be observed is, to add a very little of nitrate solution at a time, shaking violently between each dose. Finally, add five *drops*, not

* Taken from Mr. Cooper's communication to the *Photographic News* and *British Journal*.

minims, of syrupy lactate of ammonia. The emulsion may be used in about twelve hours, but gains in sensitiveness by keeping somewhat longer.

After coating with emulsion, the plate is rinsed in two changes of distilled or soft water until the greasy lines disappear; it is then soaked for two minutes in a bath or dish of the preservative, drained, and dried in the usual manner.

The preservatives he recommends are Col. Wortley's salicine, and the following:—

1	Tannin	60 grains
	Water	1 ounce
	Carbolic acid	1 drop
2	Gallic acid	48 grains
	Alcohol	1 ounce

Of these, take of—

No. 1	1 ounce
No. 2	½ „
Sugar	50 grains
Gum-arabic	50 „
Water	9 ounces

Nos. 1 and 2 are stock solutions.

The development is the same as given at page 74, or the formulæ given at page 50 will answer.

CHAPTER VIII.

CANON BEECHEY'S PROCESS.

We have now to put on record a process which is at once simple and efficient, and the thanks of the photographic public are due to Canon Beechey for its explicitness in every detail. The following is the *modus operandi*:—

Take cadmium bromide (anhydrous) ...	400 grains
Alcohol (·805)	10 ounces

and allow the mixture to stand. Decant carefully, and add eighty minims of strong hydrochloric acid.

Take of the above solution ...	½ ounce
Absolute ether (·720)	9 drachms.
Pyroxyline (as above) ...	10 to 12 grains

To sensitize this, dissolve forty grains of silver nitrate in an ounce of alcohol (·820 sp. gr.) The best method of effecting this, is to pound up the silver nitrate in an agate mortar, and to take only a quarter of the alcohol, and boil it in a test tube containing the silver salt. The alcohol will become slightly brown (due, probably, to the forma-

tion of a fulminate of silver), and should be decanted off into the bottle containing the collodion. The remaining silver should be dissolved up in a similar manner, the ounce of alcohol being just sufficient to effect solution. Between each addition of the silver nitrate the collodion should be well shaken. When the final addition is made the emulsion should be very smooth and rather thick. When poured upon a strip of glass plate it will appear transparent by transmitted light, but after keeping twenty-four hours (occasionally shaking the bottle containing it in the interval) it ought to be very opaque and creamy.

The plate having been coated with a substratum, or edged (see page 44), the collodion, which should have been shaken about half an hour* before, is poured on it in the ordinary manner, and, when set, immersed in a dish of distilled or rain water. When all greasiness has disappeared it is flooded with any of the preservatives already mentioned. Canon Beechey recommends the plate to be immersed in a dish containing beer to which one grain per ounce of pyrogallic acid has been added. The drying is conducted in the usual manner. The exposure may be taken to be about twice that which is necessary for a wet plate. Between exposure and development the plate will keep fairly for a week, but after that it seems to lose detail, and appears under-exposed.

Should the preservative on the plate be soluble in alcohol, then that solvent should first be applied to the plate (edged round with india-rubber if necessary), and

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* Canon Beechey recommends the bottle to be shaken immediately before use, and the emulsion filtered.

then be washed till all the alcohol has been removed. It is very convenient to develop these plates on a levelling-stand, in which case the india-rubber edging is a great help to keeping the solution on the plate. The alkaline development (page 50) may be used with these plates. The plates are fixed by potassium cyanide, or sodium hyposulphite (see page 57).

CHAPTER IX.

M. CHARDON'S PROCESS.

In preparing the collodion for this process M. Chardon prefers the use of two kinds of pyroxyline, both of which have previously been precipitated from collodion into water. The pyroxyline is prepared in the manner given at page 21 ; the other, the high temperature cotton, prepared as at page 24. These are mixed in the solvents to form collodion. We cannot do better than quote from an article by the Editor of the *British Journal of Photography* as to this matter, as he gives a capital description of the method to be adopted. He says :—

"Pyroxyline possessing the requisite qualities [for emulsion work] is by no means so easily obtained as the ordinary sort. Precipitated pyroxyline forms at once, if properly made, even from the cheapest materials, not only a perfect substitute for the high priced samples usually employed, but for some purposes gives an absolutely superior result.

"We commenced with a sample of pyroxyline which is sold at 16s. the pound; it is very soluble, and gives

little or no residue, but is of little use for emulsion work. Of this 400 grains were dissolved in a mixture of 10 ounces of methylated ether, s. g. ·730, and 10 ounces of ordinary methylated spirit retailed at 5s. a gallon. The resulting collodion, after standing for a couple of days, though very thick, as might be expected, was tolerably clear, except for the presence of a few floating specks and particles of dust, which was removed by passing it through muslin. This was poured into cold water, and the precipitate, when washed and thoroughly dried, weighed 368 grains, or exactly 8 per cent. less than the original cotton."

After stating that it is a wrong plan to pursue to pour the collodion gently on the water, the writer continues:

"The proper course to follow, as laid down by M. Chardon, is just the reverse of this; the collodion is poured into the water in a thin stream—preferably from a height—and is stirred vigorously during the time of pouring, and for a minute or two afterwards. By this means it is broken up into innumerable drops, each of which, immediately it comes into contact with the water, is converted into a distinct spongy mass or flock, being deprived almost instantaneously of its ether and alcohol. The stirring is continued as long as the mass exhibits any cohesive tendency, and when it feels harsh and firm to the touch it may be known that the removal of the solvents is complete. The water is then changed, the cotton passed through a cloth and dried."

M. Chardon directed one kind of cotton to be precipitated in hot, and the other in cold water, in regard to which the Editor says:—"Except in physical conditions, we cannot find, with a given sample of cotton, that it is

of much importance whether the precipitation is performed in hot or cold water.

"It is true M. Chardon directs the *coton resistant* and *coton pulverulent* to be precipitated one with hot, and the other with cold water; but it should be borne in mind that the original formulæ by which the pyroxyline is prepared differ in each case."

In order to avoid waste in washing and drying, it will be found convenient to employ a conical bag fixed upon a hoop of thin cane. When the precipitation is complete, the whole of the contents of the vessel are transferred to the washing bag, and after passing two or three pints of water through to remove the last traces of ether and alcohol, the mass of cotton is squeezed as dry as possible, and may then be removed as a lump; it is then broken down with the fingers or a spatula upon a clean porcelain dish, and dried at a gentle heat on a water bath. When quite dry, it should present the appearance of light flakes of pure white, and easily reduced to powder. It dissolves as rapidly as ordinary pyroxyline, and if carefully prepared gives at once a perfectly bright solution of a faint yellow tinge. It gives upon the glass a hard smooth film, non-contractile, and yet differing totally from the so-called powdery films commonly spoken of in connection with dry plates.

In the same article a reference is made to M. Blondeau's analysis of precipitated cotton, in which it is stated that eight per cent. of water is taken into combination. This amount of water, if it exist in the cotton, must alter the structure of the collodion in a marked way.

Be this as it may, precipitated cotton does give a very fine film; but we are inclined to think that part of the effect

is produced by the alcohol being eliminated from it *en masse*, and carrying with it that constituent of the pyroxyline which is soluble in the alcohol. This we have seen to be the case in which a finished emulsion was washed in alcohol: the resulting film having much resemblance to that of M. Chardon's. When the solvents from an emulsion are distilled over, a further alteration is effected, which renders the film beautifully structureless. The heat, no doubt, has an effect upon it.

The following account of the preparation is taken from the official report of the French Photographic Society. After stating the kind of pyroxyline to be employed, it proceeds :—

"Bromides, being always of variable purity and moisture, they undergo a preliminary treatment.

"Bromide of cadmium contains 25 to 30 per cent. of water, and it is first slowly dried by heat at a low tempeture, continually stirring it till it becomes a pasty mass. It is then allowed to fall into dried powder. Ammonium bromide is similarly dried, but at a lower temperature. This is necessary, as the two salts have to be weighed to form the double salts. The weights taken of such are in the proportion of their combining weights—that is, 272 for bromide of cadmium, and double the atomic weight, or 194, for that of ammonium." [The point to be attended to is that each shall have the same amount of bromine in combination; and since the formula of cadmium bromide is $Cd\ Br_2$, and for ammonium $NH_4\ Br$, the latter equivalent must evidently be doubled.]

The two salts are dissolved in a small quantity of water and mixed together, and these evaporated down to perfect dryness, and put away for use.

Zinc bromide is dissolved in absolute alcohol to allow the zinc oxide to precipitate. The solution is filtered and evaporated over the water bath, rather than over a naked flame, to secure perfect dryness. This very hygrometric substance must be dried immediately when it is weighed.

These salts being prepared, a salted collodion is made up as follows :—

Alcohol	1 ounce
Ether	2 ounces
Double bromide of cadmium and ammonium	14 grains
Zinc bromide	14 „
Precipitated pyroxyline, horny	7 „
Precipitated pyroxyline, powdery	28 „

A stock of this is made, and, when settled, decanted off as required. It must not be filtered, as the evaporation of the solvents is said to cause a change in the sensitiveness of the finished emulsion.

The collodion is rendered sensitive in small quantities at a time.

The silver nitrate is finely powdered, the quantities being as follows :—

Collodion	1 ounce
Silver nitrate	6·2 grains
Alcohol	3 ounces

The ordinary means already described are employed for forming the emulsion (see page 33). The emulsion is vigorously shaken in a bottle, and put aside for thirty-six hours to ripen. After this time has elapsed, about an ounce of pure distilled water is placed in a glass beaker,

and a drachm of the emulsion poured into it; after agitating the mixture it is filtered clear, which can be effected by passing it once or twice through the filter paper. This waste is tested for silver nitrate. A slight milkiness on the addition of a chloride is all that is allowable. If it shows no signs of free silver nitrate, more of the latter salt dissolved in alcohol is added to the emulsion just to give the necessary milkiness. This emulsion thus formed is next corrected by a collodion, in which cobaltic chloride is dissolved, made as follows:—

Alcohol	1 ounce
Ether	1½ ounces
Cobaltic chloride	60 grains
Pyroxyline	12 „

Of this he adds about two drachms to each 10 ounces of emulsion; as before stated in this work (page 13), all causes of fog are thus eliminated.

The novelty of M. Chardon's process is now to be explained. He takes the finished emulsion, and pours it in a fine stream into a large quantity of water. After stirring, the precipitated emulsion is filtered through a cloth, is washed carefully (the method indicated at page 40 will answer), pressed between folds of blotting-paper, and dried in the dark. This gives a flocculent powder of a clear yellow colour. To prepare the finished emulsion the following is prepared:—

Ether	½ ounce
Alcohol	½ ounce
Precipitated quinine	1 gr.

The precipitate quinine can be made from the ordinary

sulphate of quinine by dissolving it in sulphuric acid, and then adding ammonia. The precipitate thus formed is next employed.

The organic substance is first dissolved in the alcohol, and, after filtering, the ether is added. To this amount of solvents 17 grains of the dried powder is added. After some hours, when all is in solution, the emulsion is filtered through cotton-wool (see page 45). M. Chardon states that the quinine gives porosity to the film ; but it seems more probable that it acts like some other organic matters—viz., prevents a tendency to fog. The glass plate is prepared with an edging, and the collodion flowed over in the ordinary way.

The exposure is about double that required for a wet plate.

The development is made in the usual manner.

1.—Ammonium carbonate... ...	10 grains
Potassium bromide	2 „
Water	1 ounce

(Care must be taken that the carbonate is pure.)

2.—Pyrogallic acid...	50 grains
Alcohol...	1 ounce

The film is just moistened with alcohol to open the pores of the collodion, and after thoroughly washing (sufficient to cause all traces of the alcohol to be eliminated), the plate is placed in a dish containing—

No. 1	1 ounce
No. 2	10 to 15 minims

The image will appear very rapidly if the emulsion has

been properly prepared. To give it intensity the following solutions are prepared :—

A.—Potassium bromide	5 grains
Distilled water...	1 ounce
B.—Potassium bicarbonate in water...	a saturated solution
C.—Alcohol...	¼ ounce
Water	¾ „
Glucose	5 grains

These then are mixed in equal proportions—about 25 minims of each being required for each ounce of the alkaline developer. This rapidly gives the necessary density.

CHAPTER X.

DAWSON'S PROCESS.

The next process which we shall describe is one in which an "organifier" is added to the emulsion, and leads up to the more complicated form recommended by Mr. Carey Lea. We are indebted to the *British Journal Almanac* for the formulæ, which are as follows:—

Collodion.

Pyroxyline...	...	...	...	8 grains
Cadmium bromide		...	...	7 „
Ammonium bromide		...	...	2 „
Ether ·725...	...	...	...	½ ounce
Alcohol ·810	...	...	...	½ „

In practice we have found no difference in result, if ether of ·730 be used, and alcohol of ·812.

In our experience we find that the collodion should be allowed to settle some days, and then be decanted off. The pyroxyline employed may be that given at page 21.

To sensitize this a mixture is made of—

Silver nitrate	...	...	...	13 grains
Acetic acid	...	...	...	2 drops
Glycerine ...	...	...	...	1 drachm
Alcohol ·830	...	...	...	4 drachms

These are dissolved in the usual manner, it being perhaps the better plan to leave the glycerine out till the last minute. After standing twenty-four hours, two drops of hydrochloric acid are added to the above quantities, and it is allowed to rest for another twenty-four hours.

It is poured out into a dish of sufficient capacity, in order for the solvents to evaporate, and in five or six hours it is ready for further treatment. This consists in covering the pellicular mass with water for an hour, and after pouring off, covering it *for a similar time* with—

Tannin	5 grains
Gallic acid	2 „
Acetic acid	2 drachms
Water (distilled)...	1 ounce

The washing is now commenced in a manner similar to that already described at page 37, till all traces of acid are removed, which can be tested by litmus paper. When all the water is wrung out, the emulsion is dried in a hot water bath, or spread out in a warm room on blotting-paper.

The mode of eliminating all traces of water by alcohol is not admissible in this case, as it would dissolve out the tannic and gallic acid which may be left in the pellicle.

To re-dissolve the pellicle, equal quantities of ether and alcohol are used, having the same specific gravity as that given above. Dr. Dawson recommends that it be soaked in the alcohol for twelve hours before adding the ether.

The development of the plates can be carried out by the strong alkaline development (page 50).

CHAPTER XI.

CAREY LEA'S CHLORIODO-BROMIDE PROCESS.

In this process we have silver iodide emulsified with bromide and chloride, and, in some hands, it works well. The following description will show how the emulsion is prepared.

The collodion is made thus—

Ether, ·730	...	...	...	4 drams
Alcohol, ·805	...	...	...	4 „
Pyroxyline	...	...	...	8 grains

The cotton may be that given at page 21. To every ounce of collodion the following are added :—

Dried cadmium bromide	...	9 grams
Ammonium bromide	...	...	$2\frac{1}{2}$ „
Ammonium iodide	...	...	2 „

Directly before emulsifying, add—

Aqua regia	...	...	...	2 drops

The emulsion with an excess of silver is formed by adding twenty-five to thirty grams of silver nitrate ; and after an hour's interval, two grains of cupric chloride or cobalt chloride ; two drops of hydrochloric acid may be substituted for either of these, or for the aqua regia.

The emulsion may at first appear flakey, but after the addition of the chloride it is only necessary to shake well and leave it for twelve hours. On again shaking, the emulsion will be found perfect.

It may be used before drying, or after drying. In the former case, any of the preservatives ordinarily used may be employed.

If it has to be dried, it is poured out into a dish and left till it is in a leathery condition on the surface, after which a preservative is poured upon it. Any preservative will answer, but Mr. Lea recommends

Water	6 ounces
Acetic acid	3 drachms
Solution of gum-arabic with sugar	4 „
Prepared albumen	1 ounce
Gallic acid (60 grains to 1 ounce of alcohol)	4 drachms
Tannin (60 grains in 1 oz. of water)	2 „

The albumen is prepared by the addition of an equal bulk of water to the white of one egg, and clarifying with twelve drops of acetic acid.

The gum and sugar solution is made by mixing half-a-pound of gum-arabic and two ounces of sugar in forty-four ounces of water, and adding one and a-half drachms of carbolic acid.

The pellicular mass is then broken up, and it and the preservative are transferred to a large glass jar and left there twenty minutes. The preservative is then poured off, and the washing takes place as given at page 40.

Instead of drying the emulsion, it may be poured direct into the preservative, taking care that the latter is

more than four times the bulk of the former. The washing in this case takes place by decantation in the usual manner. This last method is stated to give the most soluble pellicle. The pellicle is then dried in the oven or water bath, and is re-emulsified by taking for each three ounces of the original collodion—

Ether	1 ounce
Alcohol	1 „
Plain collodion (4 grains of pyroxyline to the ounce)	2 ounces

Shake well at intervals, and in a week it is ready for use. The plate is coated in the ordinary manner, and dried. The exposure is about equal to that of a wet plate.

To develop, the plate is first soaked in a dish in a solution of one grain to the ounce of pyrogallic acid, then the development is conducted by the strong alkaline developer, page 50.

CHAPTER XII.

W. BEDFORD'S PROCESS.

At the commencement of the chapter on the preparation of an emulsion, we gave a formula which, for general work, cannot be beaten, as it is simple and very easy of manipulation. If the photographer will follow simply the rules laid down, we do not think that he will find any difficulty in getting an emulsion that will please him. This emulsion was prepared with silver nitrate *in excess*, and the excess eliminated by washing. We now quote a process given by William Bedford, which appears in the *British Journal and Photographic Almanac*. He says, after alluding to the uncertainty of the composition of the various bromides :—"Another practical disadvantage of the presence of mineral acids during the formation of an emulsion is, that they have the effect of producing the silver bromide in a state of division, coarser than is the case if they are absent."

He therefore omits all acids in the preparation, and after the emulsion is set he corrects it. This he accomplishes, after washing for two or three hours in the ordinary way, by pouring on a one per cent. solution of

hydrochloric acid, which is allowed to act four or five hours.

Now it is well known that any oxide or metal in a fine state of division (with certain few exceptions) is acted upon by hydrochloric acid. Hence by this treatment he got rid of all excess of silver, whether as oxide or sub-bromide, as chloride. He then simply presses the pellicle in folds of linen, and squeezes all excess of the solution out in a screw press, and dries.

In our own experience with this emulsion, we find it advisable to wash for a quarter of an hour with pure water, after squeezing out all excess of the acidified water. The emulsion seems to work quicker by so doing.

He states that an emulsion of this kind appears quickly under the action of plain pyrogallic acid, and may be developed to any requisite degree of density by the alkaline developer without the addition of organic matter of any kind.

He corroborates the view, held by the writer, that silver chloride in an emulsion does not need the restraining effect of an acid.

The formulæ given at page 32 may be adopted for preparing the emulsion, the nitric acid being omitted; or 4 grains of ammonium bromide may be substituted for 4 grains of zinc bromide.

This mode of preparing an emulsion is conducive to clean working and bright images, and the film seems particularly smooth and free from spots. To beginners in emulsion-work, perhaps this is the simplest form of emulsion to make.

CHAPTER XIII.

COLLODIO-ALBUMEN EMULSION.

During the past year the writer introduced to the photographic public an emulsion made with albumen, which proved to be very sensitive, and some skilled photographers were pleased with it. The process is given here, as it may, perhaps, be used as a starting point from which other emulsions may be satisfactorily deduced. In the hands of the writer the images were inclined to be thin, but when chloride is introduced it is found that this lack of density vanishes to a great extent, and leaves a very delicate and printable image. The following is the mode of preparation :—16 grains of ordinary cotton are dissolved in 6 drachms of ether ·730, and 4 of alcohol ·805, and the plain collodion thus formed decanted. 20 grains of zinc bromide are dissolved in a small quantity of alcohol, and enough bromine water added to tinge the solution with a very pale yellow. This is added to the above amount of plain collodion. For each half ounce of the above 1 grain of dried albumen is taken and dissolved in the least possible quantity of water, or eight drops of the white of an egg may be

dropped into a drachm of alcohol, and thoroughly stirred. Either of these solutions is then carefully dropped into the collodion (placed as usual in a jar), and well stirred up. This should form an emulsion of albumen in the collodion. Forty grains of silver nitrate are next added in the way pointed out on page 33, after having been dissolved in the smallest possible quantity of water and boiling alcohol. A beautifully smooth emulsion should result from this. Mr. Berkeley, who has tried this emulsion, proceeds in a slightly different way: he adds the cotton to the ether, then adds the albumen, and finally adds the amount of zinc bromide in the necessary amount of alcohol.

The amount of silver nitrate added ensures that there is an excess of at least two grains in each ounce of the emulsion.

Instead of the emulsion being made entirely with zinc bromide, greater density may be obtained by omitting four grains of it, and adding four grains of calcium chloride.

The emulsion is next poured out into a dish, and the ordinary manipulations carried out. After a couple of washings it may, however, advantageously be covered with a weak solution of silver nitrate, and again washed till the traces of silver are very faint.

The pellicle should be redissolved in equal quantities of ether and alcohol, and finally there should be about seven grains of the pyroxyline as originally used, to each ounce of the mixed solvents.

The emulsion, when finished, generally gives a tender blue by transmitted light, and is seemingly transparent. It may have a tendency to curl off the plate on drying,

in which case the addition of a little ordinary washed emulsion will correct it. It will develop with plain pyrogallic acid, and can be intensified by pyrogallic and citric acid, with the addition of a few drops of silver nitrate solution, or it can be developed by the alkaline developer, or the ferrous oxalate developer (page 51), or the hydrosulphite developer (page 54). Some photographers have found a tendency in it to form blisters when developing. This has not happened to the writer when the developer was kept above 60° F. In some hands this emulsion is extremely rapid—so much so, as to require very considerably less exposure than an ordinary wet plate.

CHAPTER XIV.

WASHED EMULSIONS USED WITH PRESERVATIVES.

Any washed emulsion may be used with a preservative which, amongst other advantages, ensures the plates being uniformly sensitive, and also ensures, with great certainty, the absence of those troublesome spots which refuse to develop. Colonel Wortley says that the thorough washing of the film prevents the formation of these spots; and Mr. Woodbury never finds them when he dries his plates rapidly and at a fairly high temperature. The emulsion used by Woodbury, however, contained resin, and it may be due to this cause that he found the absence of these enemies to emulsion work.

The simplest preservative with which we are acquainted is—

Beer	1 ounce
Pyrogallic acid	1 grain

After the plate is coated, it is washed till all greasiness disappears, and the above is flowed on the film, and allowed to remain on it for a minute. The beer solution may then be drained off, and the plate again washed, or the final washing may be omitted, and the plate be allowed to dry spontaneously. If the plate be washed, it should be given a final rinse of distilled water.

Mr. England recommends, *after* the plate with the beer preservative has been dried, that it should be washed and given a final flooding with pyrogallic acid solution, one or two grains to the ounce of water. This procedure, he says, increases the rapidity immensely: but it is rather more trouble than the methods already given.

If the beer be left on the plate, and if the dimensions of the latter be more than five by seven, a substratum (see page 43) should be used, as the films may have a tendency to blister. It will be found, however, if, *after exposure*, the plate be washed and be allowed to dry, and then be treated with dilute alcohol (page 52), and be developed, that the film will adhere tenaciously to the plate, and that no substratum will be requisite. Personally, we like this last method better than the trouble of using a substratum.

The following preservatives may also be used with the emulsion plates.

The Coffee Preservative.

1.—Best coffee	... ...	½ ounce
White sugar	... ...	90 grains
Boiling distilled or rain water	...	5½ ounces
2.—Gum-arabic	... ...	90 grains
Sugar-candy	... ...	20 „
Distilled water	... ...	5½ ounces

When No. 1 is cooled, both solutions are filtered, and the preservative applied by floating or by immersing the plate in a flat dish containing the solution.

The plate will require a substratum unless the precaution indicated above be observed.

Tannin Preservative.

Tannin (pure)	15 grains
Distilled water	1 ounce

The plate is washed, and the preservative applied as above.

Albumen Beer Preservative.

The following are prepared :—

1.—Dried albumen (or white of egg, one ounce)	25 grains
Water	1 ounce
Liquor ammonia	½ drachm
2.—Ordinary bitter beer	1 ounce
3.—Ordinary bitter beer	1 ounce
Pyrogallic acid	1 grain

The plate, after washing, is flowed over with equal parts of 1 and 2, which are allowed to be in contact with the film for one minute. It is then thoroughly washed, and flowed over with No. 3, and set up to dry.

These plates are developed by the alkaline developer given at page 50. Reducing the amount of pyrogallic acid given to one-third will cause a thin negative, which can be readily intensified by the ordinary intensifier. This preservative gives great beauty and delicacy to the negative, and subsequent intensification is better than getting density by the alkaline developer alone. The plates prepared with the albumen solution are exceedingly rapid and safe.

A substratum is required for large plates.

Red Gum Preservative.—The following alcoholic preservative may be found useful :—Australian red gum, a saturated solution, in equal parts of alcohol and water.

The plate is washed, flooded with equal parts of alcohol and water, and, after the preservative is floated on, it is dried spontaneously. The gum must be removed by alcohol and water, and the development will take place in the ordinary way. No substratum may be required. The writer has tried the above preservatives, and has therefore given them to the reader; but there is no doubt that almost any of the well known preservatives might have been applied with equal success.

As the result of hundreds of experiments, the writer has unwillingly come to the conclusion that a washed emulsion without a preservative of some kind is a dangerous process in which to place absolute trust. Films which would give perfect negatives, free from those spots which refuse to develop, may, after keeping some time, show them in perfection, spoiling every picture taken upon them. An interesting experiment is to take a plate freshly prepared, and expose half of it to sunlight to darken it, and, after the lapse of a fortnight, to expose the other half. Though the first part may show a perfectly uniform darkening of the surface, the other half will, in all probability, show the spots by their refusal to darken at all. A plate used with a preservative, on the other hand, will blacken equally after any length of keeping. The cause of these spots is rather obscure, but we think we have traced them to a quite unsuspected cause, which, if it prove correct, will indicate another use of the preservative. It must be remembered that the ordinary washed emulsion will be free from the objection if the plates are prepared one day, and exposed and developed within three or four days. This lapse of time is often sufficient for the amateur.

CHAPTER XV.

A MOIST EMULSION PROCESS.

Mr. Mawdsley, in December 1876, introduced a moist emulsion process which he states gives very certain results, and, when used with a Howard's tent, or its equivalent, is admirable, as it allows the plates to be prepared ready for use at home, and the negatives may be developed in the field with the *minimum amount of solutions*. Washed-emulsion may be employed advantageously. After coating the plate it is rinsed with water, and the following solution poured over it:—

Glycerine (Price's)	1 ounce
Albumen (white of egg)... ...	1 „
Water	20 ounces

These proportions are recommended when the plates are to be used shortly after preparation. If they are to be kept (say) a fortnight or three weeks, the following may be used:—

Glycerine (Price's)	2 ounces
Albumen...	1 ounce
Water	6 ounces

In both cases fifty grains of dried albumen dissolved

in one ounce of water may be employed instead of the white of egg. The rapidity of exposure seems to be unaltered by this method, and it may be the same as that given to the dried plate.

The development that Mr. Mawdsley recommends is as follows:—

The plate is flushed with—

Saturated solution of ammonium carbonate	1 part
Water	1 „

This is returned to the bottle for future use.

An eight-grain solution of pyrogallic acid is then poured over the plate, with a few drops of a ten-grain solution of potassium bromide to act as a restrainer.

When the details are well out, the plate is flooded with

Water	5 ounces
Acetic acid	2 drachms

This neutralizes the ammonia and arrests development. The plate is now stowed away in a light-tight box, and kept for intensification, &c., at home. If under-exposed, or properly exposed, the plate is intensified after washing and flooding with acidulated water, and fixed. If over-exposed, it is first fixed, and then intensified.

This process is simple where it is desired to develop pictures on the spot. One 4-ounce bottle, two 8-ounce bottles, and one 2-ounce bottle will contain all the chemicals and wash-water that may be required in the field in order to develop one and a-half dozen plates.

CHAPTER XVI.

MISCELLANEOUS COLLODIO-BROMIDE PROCESSES.

Under the head of "Miscellaneous Processes" we do not intend to wander into modifications of the emulsion processes, but rather to give an outline of substitutes for glass plates which have been employed from time to time.

First we have Warnerke's plan of coating textureless or enamelled paper with alternate layers of collodion and india-rubber. These latter are dilute, and two or three coatings of each are given to the paper by the ordinary method of turning up the edges of the paper to form a tray, and when supported on a glass plate applying one or other of them. After a final layer of india-rubber, the paper is coated with a washed emulsion, and allowed to dry. These sheets are joined to one another to form convenient lengths for using in what is now well known as the roller slide, by which an almost endless number of prepared films may be carried into the field and exposed without any palpable addition of weight beyond that of the camera and empty slide. The tissue is also prepared

in blocks of one dozen sheets, inserted between thin metal plates, affording a safe protection from light, and giving the necessary rigidity. In using the blocks of sensitive tissue in an ordinary dark slide, the labelled metal covering is removed, and the coloured paper between it and the first sheet is next torn away. The block is then placed in the slide in the same manner as is usual with a glass plate. Orange paper is inserted between each sheet of tissue for protecting those that are unexposed from the action of light that may possibly pass through the sheet which is being exposed.

Care must be taken that the spring in the dark slide does not bend the block. If it does, the spring must be removed, and a piece of cotton-wool substituted for it, or a glass plate may be introduced between the spring and the block.

Single sheets of tissue can also be exposed by placing them behind a glass plate, but in this case allowance must be made for the thickness of the glass whilst focussing.

The exposure is rather longer than that required with the ordinary wet process. It is, however, always advisable to over- than under-expose, as an over-exposed plate can, with proper development, be made to yield a good negative.

Previous to development, the edges of the paper are turned up to form a tray. One part of pure benzine and 10 of alcohol (methylated) are next applied to soften the collodion surface. Addition of benzine to the alcohol must never be omitted; if it is, the image will be very thin, uneven, and spotty. It also shortens the exposure. After an application for one or two minutes, the alcohol-

benzine is returned to the bottle for future use. Development of small sheets can be effected by holding them in the hand; but it is advisable, after the application of alcohol-benzine, to support a sheet above 5 by 4 on glass previously moistened with water. The water cements the paper to the glass sufficiently firmly to withstand the washing and development.

No special care is necessary to protect the back of the tissue from contact with the developer, as all stains produced by it will be in the paper, which is only a temporary support to the collodion film. If the bromide and ammonia solutions be first flowed over it, all risk of staining is avoided.

The sheet is next washed with water, and developed as given at page 50.

Warnerke recommends the following solutions to be used:—

A.—Carbonate of ammonia... ...	80 grains
Water	1 ounce
B.—Potassium bromide	60 grains
Water	1 ounce
P.—Pyrogallic acid...	60 grains
Alcohol (methylated)	1 ounce

A, B, and the water are first mixed and applied to the film; the proper proportion of P is then put in the developing cup and mixed with the first solution.

The application of this new mixture, poured back on to it from the film, will bring out the image in its full intensity.

The following table shows the proportions of solutions recommended for developing under varying circumstances. The table will be found useful for reference in other processes :—

Developer Recommended in Varying Circumstances.

	For Short Exposure in the Camera.	For Long Exposure in the Camera.	For very Long Exposure in the Printing Frame.
A	½ ounce	10 drops	1 to 20 drops
B	10 drops	10 „	10 to 20 „
P	20 to 40 „	10 „	1 to 20 „
Water	0	½ ounce	½ ounce.

The best negatives are obtained with short development; but where detail does not readily appear, more pyrogallic acid can be used.

With the developer used as above, sufficient intensity is obtained, provided the proper exposure has been given ; but if intensification is necessary, the following may be used :—

C.—Citric acid	4 grains
Water	1 ounce
S.—Nitrate of silver	15 grains
Nitric acid	5 minims
Water	1 ounce
P.—Pyrogallic acid	96 grains
Alcohol	8 ounces.

After fixing and well washing, the plate is covered with sufficient of C, and poured off and on two or three times. To every drachm of C 10 minims each of S and P are added, which rapidly intensifies the plate. All traces of the pyrogallic acid must be carefully washed from the film, and the fixed negative must be dried spontaneously.

It is remarkable that tissue negatives can stand an unusual amount of handling without injury to the collodion film bearing the image, even while still wet. For this reason the tissue can be used without varnishing, but extra protection is secured by the application of dammar in benzine, amber in chloroform, or any other varnish not requiring heat.

The negative is fixed with cyanide (page 57), and well washed. When dry, the back of the paper is moistened with a few drops of turpentine applied by means of cotton-wool, when the india-rubber and collodion film can be detached at once by a little gentle persuasion, commencing the separation by a pin or penknife blade Before separating the film from the paper, it may be protected by a weak solution of india-rubber in benzine, followed by an application of collodion made as follows :—

Ether	... 10 ounces
Alcohol (methylated) ...	... 10 „
Pyroxyline	... 150 grains
Castor oil	... 2 drachms.

The best means of preserving the tissue negatives is between sheets of plate paper. For printing, the film is cemented to a glass plate with a drop of water by squeegeeing it with an india-rubber squeegee. It can be printed from either side.

Another substitute for glass is found in the method proposed by M. Loureux, in a communication to the Belgian Photographic Association.

Paper or cardboard is waxed in the ordinary manner, and is next rubbed over with talc, when it is ready for collodionizing. To do this, alcohol is floated over a sheet

of glass rather larger than the paper, which paper is placed on the glass. After covering it with blotting-paper, a soft roller is passed over the surface to expel the excess of alcohol. (We may remark that an ordinary wooden roller covered with felt will answer the purpose; or, if a sheet of paper, also waxed, be placed over the blotting-paper, the ordinary squeegee may be employed.) The emulsion is applied, and the remaining operations are proceeded with as usual. After the preservative has been used, the paper is suspended by one corner to dry. Too thick cardboard should not be used, as it is apt to warp in drying. The paper is placed in the dark slide behind a glass plate, and then exposed. The development is conducted in the usual way, by replacing the paper on a glass plate, or by using a developing dish.

M. Loureux remarks that this negative, if printed, would show the grain of the paper; so, in order to avoid this, the film is detached after being gelatinized. The gelatine solution is prepared as follows:—

Gelatine	20 parts
Water	100 „
Glycerine	2 to 4 „
according to its concentration.	

The gelatine is first allowed to swell in part of the water, and the remainder added boiling, or solution may be effected by heating over a water bath. The glycerine is added last, and the solution is then filtered.

This solution is poured on the film at a temperature of from 85° to 95° Fahrenheit, and is allowed to dry. The film is then readily detached, and the author says that he never meets with a failure.

This process answers well, no doubt, but we should feel inclined, after getting the negative, to adopt Woodbury's plan of utilising the film for printing, viz., to coat a plate with gelatine to which a little chrome alum has been applied, and after transferring the film to gelatinized paper to bring it in contact with the gelatinized plate. In this operation the gelatine is allowed to dry, and is then immersed in hot water, and when still tacky the film is brought in contact with it by means of the squeegee, a film of water being between it and the plate. This gives a very compact way of carrying a sensitive surface in the field, and is capable of being utilised by any one.

We recommend a washed emulsion as being the most suitable sensitive compound to use.

CHAPTER XVII.

DEFECTS IN COLLODIO-BROMIDE EMULSION PLATES.

It is somewhat difficult to name the especial defects found in the emulsion dry plates, but we will endeavour to point out the principal ones.

Blisters in the film may be due to a preservative, more particularly if it contain gummy matter. Thus with the beer, or the gum-gallic, or coffee preservatives these may make their appearance. The remedy has already been given at page 100.

Black spots on development are usually due to dust being allowed to settle on the film whilst drying; decomposing organic matter in fine particles is also a fruitful source of these annoyances.

Insensitive patches or spots on development have not yet been tracked to an origin; but if a preservative be employed, they will rarely be met with.

Crape markings in the film are usually due to the solvents of the emulsion being too aqueous; or they may be due to the emulsion not having been shaken up shortly before being used.

Thin transparent films with washed emulsion are usually due to the latter cause.

The emulsion refusing to flow properly is due to deficiency of solvents. This is frequently met with if the same emulsion be used for many plates. It should be diluted down with 1 part of alcohol (·812) to 2 of ether (·720).

When the film tends to peel off the plate, the pyroxyline is probably of too contractile and horny a nature, in which case the proper treatment is to mix it with an emulsion made with one of a more powdery character.

Circular insensitive patches in the centre of the plate are sometimes met with in hot weather, when a pneumatic plate-holder is used.

The cause of fog has been pointed out in the first chapter, and need scarcely be alluded to again. To eliminate it in a washed emulsion, a few drops of a dilute solution of iodine in alcohol will prove effective. In an unwashed emulsion the addition of nitric acid will effect a cure.

Plates which fog through having been exposed to light may be rendered ready for exposure by washing off any preservative they may have on them, and immersing them in a hock-coloured solution of potassium bichromate, or by water faintly tinged with potassium permanganate, or with a one-tenth per cent. solution of hydroxyl in water. After washing, a preservative may again be applied.

Plates which fog under development, when the emulsion is not in fault, must owe this defect to one of two causes: 1st, to the light employed during development; or, 2nd, to the developer. The first cause is easily tracked, as a plate may be prepared and be developed in almost absolute darkness without receiving an exposure to white light.

If after a short application of the developer no fog is found, the light usually admitted during development is in fault. If the plate fog, the developer is wrong. In this case, try making up fresh solutions, and using more soluble bromide as a restrainer. With the ferrous oxalate developer want of bromide is often the cause of fog.

Drying markings in a film are sometimes met with. They generally form a sort of ripple marking near one edge. They are usually found when impure water is used for the final washing of a plate, and are absent if a final rinsing with distilled water be given. With plain washed emulsion these markings are never met with unless the temperature of the drying oven is high.

Thick specks in a plate are usually due to the dried emulsion from the neck of the bottle mixing with the solution and finding a resting place in the film.

CHAPTER XVIII.

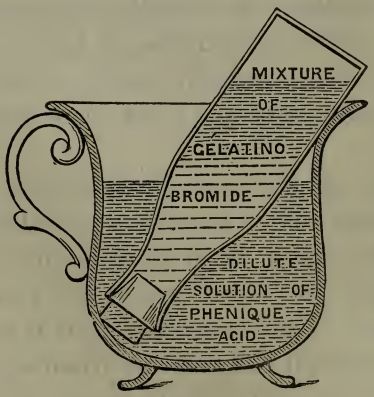
KENNETT'S GELATINO-BROMIDE PROCESS.

In the following processes we have gelatine instead of collodion as the vehicle in which the sensitive salts are held. The plates are usually extremely rapid. In Mr. Kennett's published process we have the first of the kind which became practically useful. The following is the method of preparing the gelatine emulsion according to his plan.

Forty grains of Nelson's photographic gelatine are soaked in water till thoroughly swelled, and then drained. Thirty grains of potassium bromide are next dissolved in eight drachms of water, and poured upon the swollen gelatine. The jar containing it is next placed in a can of hot water till the gelatine dissolves and a perfect mixture is obtained. Forty grains of silver nitrate are next dissolved in eight drachms of water, and poured into the gelatine mixture little by little, stirring with a rod the whole time (see page 33). The emulsion is next poured into a flat dish, and allowed to set thoroughly, and is then broken up into little lumps and covered with water, and allowed to stand for an hour, when the water is

changed, and the washing is continued for four or five hours. The wash water is tested for free potassium bromide by taking a portion of it in a test-tube, and adding a drop of silver nitrate solution to it; if present, the washing is continued till a drop of silver nitrate causes no milkiness. After thoroughly draining, the gelatine is dissolved by placing the vessel containing it in a jar of hot water, and the whole amount is, after adding one drachm of alcohol, made up to two ounces of solution.

Captain Roger Laurent has proposed a plan of keeping gelatine emulsion from decomposing by immersing the bottle neck downwards in a vessel containing very dilute phenic (carbolic) acid. The accompanying figure shows what he recommends.



There are other methods of freeing the gelatine from soluble salts which have been tried, the first of which was introduced by Mr. King. He dialized his emulsion in the usual way, as practised by chemists. This method, though scientific, is tedious, and we hardly think that emulsion makers who try the other plans will adopt it.

The other methods which we give are due to the firm of Wratten and Wainwright, and both are very easy of application, and perfectly successful. Their first plan is as follows:—The emulsion being made up as described above, and after being allowed to rest for two or three hours, two ounces of alcohol (to each ounce of water used) are poured into the bottle containing it, and well shaken up. The gelatine rapidly assumes a pasty appearance, and subsides to the bottom. The bottle is then inverted, and the fluid, which contains the soluble nitrates and excess of water, is poured off and preserved for distillation (see page 28). The explanation of the efficacy of this method is, that the alcohol has a greater affinity for water than has the gelatine, and that in extracting the water the soluble salts are extracted with it. Methylated spirit not containing gum may be used, and the lower the specific gravity the more effectual it is.

The emulsion thus freed from soluble salts may be treated with warm water, to cause it to redissolve, or it may be dried to the state of pellicle.

The second method due to Messrs. Wratten and Wainwright is that described by them in the "British Journal Almanac" for 1878, and consists in squeezing the set gelatine emulsion through napless canvas (such as is used for ladies' Berlin wool work) into water. As is well known, this method answers admirably to free salt butter of its salt, and this application to gelatine is very ingenious. The threads of gelatine are collected on a tray, and the water filtered from them by filtration through a calico bag.

We recommend that this operation be repeated a second time, using, it is almost needless to say, a fresh amount

of wash-water. Instead of this second squeeze through the canvas, the calico bag may be tied at the neck, and, with the gelatine in it, immersed in distilled water for ten to twenty minutes, when the salts will be found to be extracted. The gelatine is next scraped off the bag, and redissolved by heat.

To prepare the dry plate, the glass is first thoroughly cleaned (the method shown at page 45 is recommended), and slightly warmed, but only so much as to be pleasant to the soft part of the hand. When preparing a number of plates, the writer recommends that some large size thick glass plates be procured, and accurately levelled by a spirit-level, the horizontal position for each being obtained by three little wedges placed beneath its edge. The warmed plate is next taken on a pneumatic plate-holder, and some of the gelatine solution, filtered through fine cambric into a glass measure in such a way as to avoid bubbles (or by stretching the cambric across the lip and a portion of the top of a measure), is poured in a circular pool in the centre of the plate, and gradually made to flow to the edges. If occasion require it, the liquid may be spread by a glass rod. The surplus gelatine is now poured back into the measure, leaving sufficient of the solution on the plate, which is about three times the quantity that would be left by thorough draining. The plate is next placed on one of the levelled larger glass plates, and allowed to set. When well set, it may be removed to a tolerably level shelf, and allowed to lose moisture spontaneously. When the films have lost half their water, if possible, a current of warm air should be passed over them to increase the rapidity of total desiccation. The drying box, or the contrivance mentioned

at page 47, will answer, provided the temperature at no time exceed 100° F.

The proper equivalent of ammonium bromide may be substituted for the potassium bromide (*i.e.*, 98 grains of the former for 119 grains of the latter) in forming the emulsion; and it may also be prepared with an excess of silver nitrate. A slight excess is safest, forty-six grains being substituted for the forty grains above; but, on the whole, the excess of bromide gives most reliable plates, since the addition of acid is almost inadmissible, and there must be a liability to fog from the cause stated in the first part of this work.

It has been proposed to substitute for half the amount of water used in dissolving the gelatine the same quantity of mild ale, or of a coffee solution, but we doubt whether it has any advantages, and the simplest process just given is recommended for good ordinary plates.

Mr. Kennett has simplified the manipulations for dry plate makers by drying the gelatine emulsion after washing, and issuing it in the form of a pellicle. The mode of drying he has patented. To form an emulsion from the pellicle, 50 grains of the latter are dissolved in 1 ounce of water by aid of heat. After soaking for a quarter of an hour, and filtering through muslin, the emulsion is ready to use.

The exposure is about equivalent to that necessary for wet plates.

For developing these plates the following solutions are required :—

1.—Pyrogallic acid	4 grains
Water	1 ounce

2.—Ammonia (·880)...	½ ounce
Water	8 ounces
3.—Potassium bromide ...	...180 grains
Water	8 ounces
4.—Gelatine	... 20 grains
Water	... 10 ounces

For development the plate is first soaked for five minutes in distilled water in a dish, and then, for half a minute more, after adding half to one ounce of No. 4 to the water; it is next drained, and then a mixture in the proportion of half-an-ounce of each of No. 2 and No. 3 to each ounce of No. 1 applied. The image will appear rapidly, and gain in strength; any amount of density may be obtained by adding one or two drops of No. 2. The plate is fixed in sodium hyposulphite (page 57).

Mr. Kennett's latest mode of development differs slightly from the above, though the same solutions, except No. 4, are required.

The plate is placed in a dish, in which enough of No. 1 is placed to cover it. After a few seconds, the solution is poured into the developing cup, and to every 30 parts of No. 1 used, 2 parts of Nos. 2 and 3 are added. The mixed solutions are poured on the plate in the dish, and two or three drops of No. 2 are added to give density.

In case density be deficient, Mr. Kennett recommends:—

Pyrogallic acid	3 grains
Acetic acid	6 drops
Citric acid	1 grain
Water	1 ounce

This is flowed over the plate, and then two or three drops of a twenty-grain solution of silver nitrate are dropped into the cup ; the solution is then poured back on to the plate, and density will be rapidly obtained.

The colour of the negatives is usually of an olive colour, and very non-actinic, hence care must be taken not to push the density too far.

The preparation and development of the plates should take place in any subdued light, as they are extremely sensitive to weak radiations. Blisters and frilling of the edges sometimes make their appearance. Hard water containing sulphates are said to obviate this evil, and it has been proposed to soak the plates in a solution of Epsom salts as a deterrent.

CHAPTER XIX.

BENNETT'S GELATINO-BROMIDE PROCESS.

Mr. Bennett has recently described a method of preparing plates by which extreme rapidity is secured. The following description of it is extracted from the *British Journal of Photography*, as he describes it, as much stress is laid on following strictly the directions laid down. The writer has worked the process from the description given. Mr. Bennett says:—

"First, then, the light. I have tried 'warranted non-actinic,' and 'tested by spectrum analysis' glass, and can print transparencies through two thicknesses of such in about thirty minutes. Procure, therefore, from a glass merchant, some of the *darkest* shade of ruby, and use two thicknesses for daylight and one for lantern. This is positively necessary, as we are to use a very powerful developer upon a very sensitive plate. If gelatine workers were careful on this point I think we should hear less of 'organifiers' or 'want of density' than at present. I never have any trouble on that score, because no actinic light having touched the emulsion I

can apply any amount of development without any danger of fog.

"To make 'assurance doubly sure,' use a ruby-coloured hock bottle, and with two eight-ounce decanter-shaped bottles made of test-tube glass to stand heat—procurable at Rouch's, and, doubtless, elsewhere—weigh out for a ten-ounce solution—

Ammonium bromide	70 grains
Best silver nitrate	110 „
Gelatine	200 „
Distilled water	6 ounces

"Use Nelson's 'No. 1, photographic gelatine,' for with the opaque sixpenny packets you have irregularity, red fog, and frilling. Place aside four ounces of water for the bromide, and two ounces for the silver; dissolve the bromide with heat in one of the test bottles in one or one and a-half ounces of water; pour into the hock bottle; swill out the test tube with the remainder of the four ounces set aside for the bromide, and also pour in. I do it by heat to ensure all being dissolved, as it does so very slowly after the gelatine is inserted. The four ounces of solution being now almost cold, add the gelatine, shake up well, and place in two or three gallons of water at 90°. I use a fish-kettle with lid. [A good-sized saucepan with a lid answered perfectly with the writer.] In two hours the bromized gelatine will, after well shaking, be quite liquid, and also nearly at 90°. Now dissolve the silver in the other test bottle by heat in one ounce of water, cool to 90°, and pour in; use the remainder of the two ounces set aside for the silver to swill out, heat to 90°, and pour in. By being so parti-

cular we get regularity, and are able to mix the plates of different batches, which is a great boon. Shake the emulsion very briskly, and replace in the kettle for two, four, or seven days, according to rapidity required. The temperature should never be over 90°: if you do not let it exceed that you will not have red fog. 'Cosy,' it up with flannel, and it will not lower many degrees during the night. I, however, use a stove two feet across, and place it on that; a faint gas jet below keeps it always at 90°. I shake up every twelve hours. If washed in two days, the emulsion is rapid and dense; in four days, more rapid and less dense—quick enough for any drop-shutter known, when developed as below. With some that I kept for seven days, with drop-shutter on a dull February morning, pebbles close to the camera were perfectly exposed. The negative was thin under ammonia, but bore intensifying to any extent.

"Cool the emulsion in a bottle not smaller than a Winchester quart, and wrap it up in brown paper to exclude all light except the lip of the neck. Let an india-rubber tube go quite to the bottom of the bottle to stir away those layers of water which, on account of greater specific gravity (by reason of the salts they now contain) would otherwise remain there. Wash for twelve hours; a dribble is sufficient. Upon melting you have eight or nine ounces of emulsion; add three-quarters of an ounce of pure alcohol heated to 90°; fill up with water (also warm) to ten ounces, and coat (see page 118). The plates should be only lukewarm, or you will have red fog. For beginners it much helps the coating to double the quantity of alcohol, leaving out water to that extent. The operator should not be alarmed at the peculiar mottling

of the film (due to the alcohol) directly after coating; this subsides in a few seconds to an even surface. The extra alcohol does not appear to alter the sensitiveness, and is a great help; but with experienced workers it is not necessary, and the quantity mentioned at page 124 is sufficient to draw the emulsion up to the edges, which is the sole object of introducing it. When no alcohol is used you always have *thin* edges, which is very objectionable, as the negative, of course, will print dark at those parts, and this small addition of alcohol totally rectifies this fault. It is difficult to measure the exact quantity of emulsion required for each plate; one ounce would probably cover *eight* plates of $6\frac{1}{2}$ by $4\frac{3}{4}$ size.

"By darkening a good-sized room temporarily for coating, it obviates the necessity of a drying-box, for if the films can lie on the table for twelve hours they will be dry, or sufficiently so to stack up in an ordinary box. Expose a few plates with small stops—instantaneously; gradually increase the size of stop or length of time.

"To develop I use for $6\frac{1}{2}$ by $4\frac{3}{4}$ one ebonite tray $8\frac{1}{2}$ by $6\frac{1}{2}$ for ammonia, one ditto for silver, and one 10 by 8 to cover over either during development to keep all light off. After soaking a minute, pour the following quickly along that side of the tray which is not occupied by the plate, and by rocking the dish suddenly send it sweeping over the plate (it is developed in five to twenty seconds):—

Pyrogallic acid...	1 grain
Bromide	*none*
Pure undiluted liquid ammonia	1 to 10 drops
Water	1 ounce

Do not flood with pyrogallic acid first, or you will render the plate slower; nor add more pyro, or you will again slow the plate, and, moreover, have it too dense. If the exposure has been sufficiently short, you should have a dense negative, with bare glass for shadows, almost as soon as the developer has covered it. A 10 by 8 Dallmeyer triplet, with drop-shutter, would require in good light (say) four drops of ammonia; if bad light, eight to ten drops. A six-inch single lens, in good light would require (say) one drop; in bad light, four drops. If much ammonia be used, and the plate be not developed in half a minute, make fresh developer, and wash the plate.

"Being now in possession of some extra-sensitive plates, put one in a thick book, and, having placed it five or six inches from your ruby glass window or lantern, draw out the plate one-third for a few minutes; again draw it out further one-third more for a short period. You will then have the film in three divisions, as it were—one portion not having been exposed to the red light, and the other two portions having had different exposures. Now develop, and use (say) three drops of ammonia. If your light be still at fault, the exposed portions of the plate will fog; in that case, use another thickness of ruby glass."

APPENDIX.

SINCE the foregoing pages were printed some new formulæ have been given to the photographic public, and in this Appendix they will be found.

MR. H. COOPER'S COLLODIO-BROMIDE RELIABLE DRY-PLATE PROCESS.

In the paper communicated by Mr. Cooper to the Photographic Society of Great Britain, he says, regarding this process: "Whatever may be the cause of spots on a plate, the use of a preservative in the preparation of the plate will entirely prevent the appearance of the pests, and I am much pleased to be able to give formulæ by which films possessing the following most desirable qualities may be produced with certainty and rapidity. First, the quality of image is almost perfect, much resembling that given by a really good collodio-albumen plate. Secondly, the films will keep for a lengthy period without deterioration, both before and after exposure. I exhibit a negative which was kept five

months before exposure, remaining for three months in a dark slide, and carried about on long journeys, being submitted to many variations of temperature and hygroscopic conditions of the atmosphere. After exposure and before development it was kept five weeks. Other plates have been kept three months after exposure. I give these data as many folks' ideas of a 'lengthy period' are various. I have plates prepared early this year which I am keeping on to test from time to time.

"In exposure, very great latitude is allowable—an unspeakable boon to the photographer on a tour, with no conveniences for developing a trial plate from time to time. This last summer I took a number of plates away with me on a three months' outing, and exposed some of them from time to time on a variety of subjects, and many times felt quite at sea as to the proper exposure to give; and yet on my return home I developed every plate I had exposed into a decent negative.

"Another point of importance is that the development is simple; entirely under control; and the most varied effects may be produced during its course by judicious use of the powers alkaline development gives us. Some may think it rather late to bring forward a slow process in these days of extra rapidity; but I, for one, require plates that give me *pictures*, and I must have materials over which I can exert some influence during the progress of the chemical changes which produce the visible image. I must be able to modify the action of the developer, both generally and locally, and so be able, to a certain extent, to raise the production of a negative from the region of mechanics to that of art. This we cannot do at present with gelatino-bromide plates, and until the extra-rapid films are as much

under control as the slower collodio-bromide, I shall surely keep to the latter for general work, reserving the 'rapids' for special and exceptional cases."

Mr. Cooper's formula is as follows :—

"Prepare first a stock of plain collodion by dissolving 160 grains of ordinary pyroxyline* in six ounces absolute alcohol and ten ounces ether. Good methylated alcohol will answer for these first solvents, as also ether s.g. 730, purchasable at 1s. 6d. per lb. Also make an alcoholic solution of zinc bromide, 80 grains to the ounce. Even after filtering, this solution will throw down a deposit upon keeping, and this must be carefully left undisturbed. To make 10 ounces of washed emulsion, take 5 ounces of the above collodion, and add to it one ounce of the zinc bromide solution, and 20 minims of syrupy lactate of ammonia.† Sensitize with 150 grains of silver nitrate, dissolved first in 80 minims of water, and then in 3 ounces strong alcohol. Boil together, and add it to the bromised collodion at once. I attach importance to the addition of the boiling solution, so as to raise the temperature of the mixture, and when only a small quantity (such as the above) is made, I take the precaution to wrap the bottle in a thick cloth to retain the heat as long as possible. On examining the portions just given, it will be seen that the silver nitrate is

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* Mr. Cooper recommends the pyroxyline as prepared by Hopkin and Williams, as answering the purpose.

† "Some experiments made since this paper was first written go to show that a great gain in sensitiveness may be obtained by reducing the proportion of plain collodion. I have tried three ounces, and even two ounces, instead of the five, with the most encouraging results. I am indebted to leaders in the *British Journal* for the suggestion."

decidedly in excess, and that the alcohol is used in larger proportion than usual.

"Lactate of silver has long been a favourite addition of mine to emulsions, and I am more than ever pleased with its action. I must call attention to a curious effect which is produced if the bromised collodion is allowed to stand many minutes after the lactate is added, and before the sensitizing. The collodion becomes quite milky, and throws down a crystalline deposit. It is well to add the lactate immediately before the silver, or even to defer putting it in until after the sensitizing. I cannot pretend to say what chemical or physical effect occurs in the 'lactised' collodion: I merely mention the fact.

"The emulsion is ripe in about twenty-four hours; but I am disposed to think it an improvement to keep it for a longer time, up to three days. At the expiration of the ripening period, twenty minims of strongest nitric acid are to be added, and the emulsion well shaken. I prefer to add the acid just before the washing instead of at first. I believe a better film is given by so doing.

"We are now faced with the question of how best to wash the emulsion. Shall we pour it out and evaporate the solvents, or precipitate it? From a lengthened experience of both methods I cannot recommend precipitation, except in cases where the finished emulsion is to be used up within a month. It is now a generally acknowledged fact that precipitated emulsions will not keep well. But where large batches of plates can be prepared at a time, and no waste occurs, I can speak to the good qualities of the emulsion when precipitated by mixing it with twice its bulk of the following organi-

fier, and when the pellicle has fully separated and set, washing for some time in water containing a little nitric acid (half-ounce to one gallon), and finally in several changes of pure water. The mixture—

Tannin	... 500 grains
Gallic acid	... 200 „
Grape sugar	... 200 „
Strong acetic acid ...	... 10 ounces

or a proportionately lesser quantity of glacial, to be dissolved in water, and make up to 100 ounces. This method is expeditious. The alternative, and I think the better plan, is to pour out the emulsion into a sufficiently large dish (1 ounce to 25 square inches, or say 5 ounces in a 12 by 10 dish). Evaporate the solvents more thoroughly than usual; in fact, the pellicle may be allowed to get almost dry. Wash first in water containing half-an-ounce of nitric acid in one gallon of water, and then in plain clean water for some considerable time. If the water in use is hard, distilled water should be used at first and lastly. Wash thoroughly. The extra drying of the pellicle and the large proportion of alcohol it contained will materially assist in shortening the time. When dry, dissolve the above quantity of pellicle in 5 ounces of pure absolute alcohol, and a like quantity of extra purified methylated ether, s.g. 720. An emulsion prepared in this manner with the lactate of ammonia will give excellent negatives without further preparation if the plates are used at once; but its subsequent treatment with alkaline albumen gives the especial qualities for which I so greatly value it. The plates are much quickened by the after treatment. This particular emulsion

has its sensitiveness doubled, whilst some others are rendered slower."

Mr. Cooper then describes gelatinizing the plates with gelatine and chrome alum as given at page 44. He says that small plates may have an edging only (page 43), but that he prefers giving them the full coating:—

"Coat with the emulsion. When well set, immerse in water. I, myself, use a grooved box, well coated with shellac, and when I have coated and immersed as many plates as I intend to prepare, I cover up the box and thoroughly ventilate the room, so as to get rid of all fumes of alcohol and ether before proceeding further. I see no reason why a tin box with removable grooved pieces, similar to the one sent out by the Autotype Company for developing chromotypes, should not answer. Of course it must be kept for this purpose alone.

"The plates are now to be flooded with the alkaline albumen, or dipped in a bath of it. In either case the albumen must be in contact with the film for at least a minute. The plate is then to be thoroughly washed, flowed with a preservative, drained, and dried. After backing it is ready for the camera. The albumen may be prepared in bulk, either with whites of eggs, or with the pure dried preparation. Of the latter dissolve 60 grs. in 3 ounces of water, and add 1 drachm of strongest liquor ammonia ·880. If white of egg be used, first pour in a few minims of dilute acetic acid, and well stir. In two or three hours strain, and to each ounce add two of water and one drachm of liquor ammonia.

"For the 'preservative' I have tried a host of substances, and find the simplest of all to be the best—viz., a two-grain solution of gallic acid. For the sake of

constant uniformity and certainty, I was anxious to discard from my formulæ all compounds of uncertain chemical constitution, such as beer, or even tea and coffee, or else I could, from my own experience, speak strongly in favour of a decoction of tea, made by boiling 1 ounce of compressed black tea in 4 ounces alcohol and 12 ounces water. One ounce of this is diluted with 10 ounces of water to form the final coating for the plate. It is of importance that the plates should be thoroughly dried, especially if intended for packing; as although these plates will stand exposure to a moist atmosphere better than most others, any damp remaining in the films when they are stored away will be a source of future trouble."

Mr. Cooper recommends a full exposure in the camera for these plates. We have found that with a stop $\frac{f}{20}$, and in an open landscape and good light, thirty seconds is ample; but that three minutes may be given without detriment. In regard to development he says:—

"Beware of strong pyro. Use it very weak to begin with, from one-fourth to one grain per ounce, and add carbonate of ammonia and bromide of ammonium as the exigencies of the case may require. For a $7\frac{1}{4}$ by $5\frac{1}{2}$ plate I usually begin with an ounce of water with half-grain of pyrogallic acid, one drop of a saturated solution of ammonium carbonate, and a like quantity of a 10-grain solution of ammonium bromide.

"Use patience, and do not hurry the development.

"When all the details are out, a little stronger pyro will give plenty of intensity. Beware of making the image too intense; this is easily done.

"By pouring the developer repeatedly from the measure upon one spot, especially if a little extra ammonia be used, local detail may be coaxed out, and by employing the same plan with stronger pyro local intensity is easily obtained.

"With these plates the developer may be used almost like a painter's brush, and it is only by the intelligent and artistic use of all such means to an end that *pictures* such as a true artist would value can be produced by means of the camera."

MODIFIED PROCESS WITH WASHED COLLODIO-BROMIDE AND BEER PRESERVATIVE.

Mr. William Brooks, in the PHOTOGRAPHIC NEWS, has recently described a modified method of applying the beer preservative to washed emulsion plates. At page 99 we have given a formula from which the following differs but slightly.

The albumen giving the substratum is prepared according to Ackland's once well-known formulæ, and is as follows:—

The whites of *fresh* eggs are collected, and to every 8 ounces, 1 ounce of water and 24 drops of glacial acetic acid are added by pouring it into the albumen in a fine stream, and stirring eventually with a glass rod for one or two minutes. The albumen should on no account be beaten or whisked up, or the resulting preparation will be milky. It is allowed to rest one hour or more, and then strained through coarse muslin or cheese-cloth. To the strained albumen is added one drachm of the strongest liquor ammonia (·880), when it can be put away in corked bottles and kept for use.

Mr. Brooks uses this as a substratum for the plates as well as in developing. For the former purpose he takes—

Prepared stock albumen	...		...	1 ounce
Water ...	...	...	...	1 pint

This is applied as given at page 45. Any ordinary washed emulsion (preferably one of good body and yielding an opaque film) can be employed. The plate is coated in the usual manner, and when properly set it is, *without washing*, plunged into a bath made as follows :—

Bitter ale	...	...	...	1 ounce
Pyrogallic acid ...		...	...	1 grain

Sufficient of this being used to fill a dish, into which the plates are placed, to a depth of half-an-inch. The ale should not be of the kind known as sweet or mild, as both these contain too much saccharine matter. The plate is left in the preservative till there is no repellant action due to the ether and alcohol. It is then taken out and dried spontaneously, a final warming being given to it by means of a drying oven or a hot water tin previous to storing. The plates do not require backing unless the emulsion be thin. The exposure necessary must be ascertained by a trial plate.

Mr. Brooks' method of development he describes as follows :

"*Development.*—After the plate has been exposed, take it on a pneumatic holder, and flow over it equal parts of alcohol and water. I must here add a caution not to use the alcohol too strong, or it will attack the film unevenly and cause mottling, especially in the high-lights, as I am sure, from past experience, this is one of the causes. It is

not seen so much in the half tone, and scarcely at all in masses of foliage, or where the subject is well broken up. If mottling does occur, it is most at the thick end of the plate. I do not know if this corresponds with the experience of other workers. If the alcohol is used without diluting (say of a s.g. of ·825) the mottled markings are very large, and as the alcohol is diluted with water, they become smaller and smaller till they disappear altogether. I generally allow it to soak well into the film for about two minutes, of the strength mentioned above (half water and half alcohol). Methylated spirit answers every purpose, providing that it is free from gum (if contaminated with gum, it turns milky on the addition of water). If a quantity of plates are to be developed, I prefer to immerse each plate in a tray containing the spirit, as it is then done effectually. The plate is then taken and allowed to soak in a dish of clean water, and rocked about until the water flows evenly over its surface. Previous to applying the developer, flood the plate with the following—

Stock albumen (as above) ...	1 part
Water	4 parts

Allow this to soak well into the film; well rock the plate to ensure even action; not less than one minute must be allowed for this part of the operation. The plate is then slightly drained, and the alkaline developer applied, made from the following stock solutions—

P.—Pyrogallic acid (best) ...	96 grains
Absolute alcohol	1 ounce
A.—Sat. sol. ammonium carbonate	4 ounces
Potassium bromide	2 drachms
Water	8 ounces

A few drops of solution P for 9 by 7 plate (say five drops), and one ounce of solution A, are mixed in a perfectly clean measure, and at once poured over the plate; as soon as it is covered it must be rocked vigorously for a few seconds, so as to make it blend with the albumen on the plate, and if the plate has been properly exposed the image will at once make its appearance, gradually acquiring intensity.

"After the developer has been on for some little time, should it apparently cease in its action, drain it off, and again apply a little of the prepared albumen solution for about half a minute; drain again, and apply the alkaline developer as before: the image will then, perhaps, rush out very rapidly. This method can be repeated as often as necessary; but, as a rule, with a properly exposed plate, one application of the albumen is sufficient. If more density is required, a drop or two more of P solution can be added. If too much pyro is used, a very hard negative is the result, so it must be used with judgment. I have actually developed a 24 by 18 plate to full printing density with only half a grain of pyro. The formula given for solution A is given for work under normal conditions. In the winter time the bromide can be reduced one-half, and in very warm weather it can be increased.

"I have used the albumen as given above for several years, and the more I use it the more I like it, as it gives an image so much like a good wet plate taken under the best conditions.

"Should it be desirable, the intensity can be brought up in the ordinary way before fixing with acid pyro and silver, same as for wet plates. The plate must be well washed to free it from all traces of ammonia, and before

the silver is added to the acid pyro it is first applied to the plate alone, which will generally be sufficient to neutralize whatever may have remained in the pores of the film. The plate is then fixed in the ordinary way with—

Sodium hyposulphite	2 ounces
Water	1 pint

and then well washed.

"I also, whenever I use hyposulphite for fixing, especially for those films which are very porous, allow the plate to soak in plenty of water for half-an-hour to get rid of all traces of it. The plates require to be dried spontaneously, and then varnished in the usual way."

Mr. Brooks states that he has kept plates prepared by this formula five months before exposure, and about the same time between exposure and development, and has developed them without stain or speck.

COLLODIO-BROMIDE EMULSION WITH EXCESS OF BROMIDE.

The writer, in some recent investigations, was led to the conclusion that, theoretically, the loss of sensitiveness due to using a collodio-bromide emulsion with an excess of soluble bromide must be due to the want of a bromine absorbent; and that if, with an excess of soluble bromide, we had the presence of such an absorbent, that then the sensitiveness should be in a great measure restored. When light causes the liberation of bromine from the silver bromide (see page 9), and when a bromine absor-

bent, such as potassium nitrite, is present, we have the following reaction :—

Bromide and	Potassium Nitrite	and Water give	Hydrobromic Acid	and	Potassium Nitrate.
$2Br$ +	KNO_2 +	H_2O =	$2HBr$ +		KNO_3

The hydrobromic acid liberated would have a tendency to destroy the image; hence it is desirable that a neutral compound should be formed. This will be the case if an alkaline carbonate be added, for then we have—

Bromine	Potassium Nitrite	and	Sodium Carbonate	give	Sodium Bromide	Potassium Nitrate	and	Carbonic Anhydride
$2Br$ +	KNO_2 +		Na_2CO_3 =		$2Na\,Br$ +	KNO_3 +		CO_2

This practically was proved to be the case. In making a washed emulsion with excess of bromide, it will be well, then, to add to every ten ounces of emulsion two drachms of a saturated solution of potassium nitrite in alcohol, and to apply to the film sodium carbonate in the first wash water, and then to wash again. By this means the retarding effect of any trace of soluble bromide left is counteracted by the presence of the trace of potassium nitrite and of sodium carbonate.

LANTERN SLIDES AND TRANSPARENCIES.

Mr. W. Brooks, writing to the PHOTOGRAPHIC NEWS, gives a method of preparing lantern slides and transparencies, an abstract of which is as follows :—A washed emulsion containing silver bromide alone is employed, which should be a little thinner than for ordinary work, as a finer result for this class of work is thereby obtained. Flattened crown glass of medium thickness is soaked in any mineral acid for an hour, and is then washed under the

tap, and polished with a little methylated spirits and chamois leather. Each plate is edged with india-rubber in benzole, about one-eighth inch all round—[we find that French chalk dusted over the plate saves this edging]—coated with the emulsion, and allowed to dry spontaneously. No preservative should be used, since with it toning becomes difficult. If the negatives are large, they must be printed in the camera; if of ordinary density, in ordinary daylight; but if of a very intense character, sunlight diffused by ground glass is absolutely necessary. The exposure varies, of course, with the brightness of the light used, varying from twenty seconds to three minutes, but plenty of exposure should be given in any case. To develop, the following solutions are employed—

A—Saturated solution of ammonium carbonate	4 oz.
Potassium bromide	2 dr.
Water	8 oz.
P—Pyrogallic acid	96 grs.
Absolute alcohol	1 oz.

For a quarter-plate 2 drops of P are added to 2 dr. of A, and poured over the plate at once, the development taking place by preference in a glass dish a little larger than the plate. Should the subject be one of violent contrasts, 1 drop of P is sufficient, whilst with a weak negative 5 or 6 drops may be used. The image must be developed to its full intensity, and is then fixed in

Potassium cyanide	20 grains
Water	1 ounce

Sodium hyposulphite is useless in this case. The image must be cleared, and then *well* washed.

The toning agent employed is platinum tetra-chloride.

Platinum tetra-chloride	... 2 to 4 grains
Water	... 20 ounces

[In our own practice we have found the addition of about 6 drops of nitric acid aids the toning.]

The colour of the deposit changes from orange to pale claret, then to deep claret, next to the ordinary photographic purple tone, and finally to a slaty black colour. The action may be arrested at any stage. If the washing after fixing be incomplete, it will tone in patches and prove unsatisfactory. If the image be found too intense, it may be passed through the cyanide solution again. This destroys the warm tone, but has little effect on the black tones beyond reducing the intensity. The toning can be performed in daylight. If the action be too vigorous, the solution must be diluted with water. When dry, the plate is varnished with—

White hard varnish ...	... 1 part
Methylated spirit ...	... 3 to 6 parts

The latter quantity depending on the thickness of the former

RAPID PREPARATION OF GELATINO-BROMIDE PLATES.

The writer has found that a great facility in obtaining density is secured by emulsifying rather more silver bromide in a given quantity of gelatine than is usually recommended. The formula employed is as follows:—Gelatine (Nelson's photographic) 40 grains. Water sufficient to cover it in a beaker.

The swelled gelatine is drained, and 60 grains of potassium bromide are added to it dissolved in 1 ounce of water, together with 10 grains of potassium nitrite, in order to counteract the retarding action of the potassium bromide. This is gently heated till the gelatine dissolves, when 80 grains of silver nitrate, dissolved in 1 ounce of water, are added in the usual manner. The emulsion may now be kept warm up to 90°, according to Mr. Bennett's plan, for any time that may seem best, and may be washed, if thought desirable, and allowed to set, and the plates treated with alcohol. It may then be re-dissolved and filtered, and when cooled to about 80° is ready for coating a plate. This is done in the usual manner, and the plate is laid upon a levelled shelf to set well. If the emulsion* have not been washed, the plate, when the film is set, must be placed in a dish of water for a few minutes, to get rid of the excess of soluble salts, and then in a second dish for a few minutes more. It is next immersed in a bath of methylated spirits free from resinous matter, and allowed to soak for half-an-hour, after which it is set up to dry in a cupboard. After half-an-hour's draining it may be placed in a hot-air oven, and in a quarter of an hour or so it will be ready for use. It is, however, preferable to let the plates dry spontaneously, as the gelatine is less liable to frill. This method of preparation is about the most rapid that can be adopted, and certainly the plates are very sensitive. It may pertinently be asked if there is any advantage in using an unwashed emulsion. If plates are required in a hurry, there evidently is an

* It must be distinctly understood that washing the emulsion is most desirable, and should only be omitted under a press of time, since the plates are not so rapid nor set so evenly when coated with unwashed emulsion.

advantage, since the time expended in washing the pellicle is thereby gained. Another point, however, is this: if the emulsion be *kept* in an unwashed state, it does not readily decompose. When potassium bromide and silver nitrate are used, we have potassium nitrate left in the gelatine; as every one is aware, saltpetre preserves organic matter, hence it protects the gelatine in this case. It would seem that directly a plate is set, and washed in fresh water, if immersed in alcohol, the danger of the gelatine decomposing is very considerably reduced, and we can therefore hope that one source of annoyance in the preparation of such plates may be overcome.

In developing either by the alkaline or ferrous oxalate developer, the writer always uses a small quantity of soluble bromide. It may cause a necessity for a slightly longer exposure, but by its use there is certainly a gain in clearness.

A CONVENIENT PLAN FOR WASHING GELATINE EMULSIONS.

In Mr. Bennett's process a rather inconvenient plan of washing the gelatine emulsion is prescribed, and one on which we think we have improved, since by adopting it the emulsion can be washed in an ordinarily lighted room. A bottle (by preference having a wide neck) is chosen, and a tin canister with a top is procured, into which the bottle can be placed and covered up. In the top a hole is carefully drilled, so as just to fit a piece of $\frac{1}{4}$-inch glass tubing, $\frac{1}{2}$-inch longer than the canister is high; and about 2 inches from the bottom another hole is bored, and a $\frac{1}{4}$-inch tin tube, with a couple of bends at right angles to one

another, soldered over the hole. The bottle with the emulsion in it is placed in the canister, the glass tube put into the bottle through the hole in the lid, and a piece of India-rubber tubing slipped over the projecting end of the tube till it fits tightly against the lid. The other end of the India-rubber tubing is fitted to the water supply, and the amount of water admitted to the bottle regulated by a clip on the tube or by the tap. We have ourselves used as a reservoir a 4-gallon jar with a bung-hole at the bottom; into the bung a piece of glass tubing is inserted as an exit for the water, and the supply is controlled by a clip on the India-rubber tubing. It answered excellently: four times filling washed the emulsion perfectly.

A CONVENIENT PLAN OF MAKING FERROUS OXALATE DEVELOPER.

Take a saturated solution of neutral potassium oxalate, and an equal quantity of a saturated solution of ferrous sulphate, and mix the two; the resulting fluid will be ferrous oxalate dissolved in a solution of potassium oxalate, and potassium sulphate. The two may be mixed immediately before use, and, if warmed, will speedily assume the deep red colour indicative of the ferrous oxalate, leaving a slight precipitate, which can be filtered out.

FORMULA FOR FERROUS OXALATE DEVELOPER.*

Oxalic acid	13 ounces
Potassium carbonate ...	16 oz. or thereabout

* Kindly furnished by Mr. J. W. Swan.

These are each made into saturated solutions, and added till the neutral oxalate is produced.

One ounce of ferrous sulphate is precipitated by oxalic acid, and the ferrous oxalate washed and added to the above, the whole making up to eighty ounces with distilled water.

PACKING DRY PLATES.

To pack dry plates, resort may be had to the plan of separating one from the other by two strips of cardboard or thick paper bent zigzag (as a hem is prepared for stitching), one at each end of the plate. Between each fold is placed a dry plate; the whole bundle should be bound round with twine, and wrapped in non-actinic coloured or opaque paper. A slightly different method is practised by Mr. Gordon and Mr. H. Cooper. Strips of cardboard a quarter-inch wide and of the length of the plate are cut and glued on a piece of silk, strong muslin, or other flexible material, about one-eighth of an inch apart. When dry, cut the cardboard along the centre, thus leaving pairs of strips of cardboard one-eighth inch wide glued on to flexible material. The space between the card should be equal to the thickness of two plates put back to back. To pack the plates, lay one on the table face up; then one of the card guards at each end; then on this a pair of plates back to back; then turn over the other part of the guard, and place two more plates, and so on, finishing with a single plate. The plates are then tied together, and packed in sheet gutta-percha, and next in tinfoil, though we have found that well varnished black paper answers in lieu of them both, if the packet be first wrapped in orange paper.

The packages when broken into can be stored in any of the well-known dry-plate boxes.

COLLODIO-BROMIDE EMULSION WITH GUM GUIACUM.

A very favourable opinion has been formed by the writer of the addition of gum guiacum to a washed emulsion. The plates keep well, are free from spots, and develop with great softness. This addition to an emulsion which is inclined to give a horny film is most valuable, as the collodion has no tendency to leave the plate under development, and the developer is able to permeate the whole thickness of the film; no substratum or preservative is required, and blurring with a thin emulsion is much mitigated.

The following formula will be found suitable :—

Washed emulsion	3 ounces
Boiling alcohol, saturated with gum guiacum, then allowed to cool, and filtered	½ ounce

The plate is coated as usual, and may be dried in a hot air oven or spontaneously. The application of a gentle heat is, however, recommended.

TABLE SHOWING SP. GR. OF ABSOLUTE ALCOHOL WHEN COMBINED WITH VARYING QUANTITIES OF WATER AT 60° F.

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
50	·9228	85	·8357
55	·9068	86	·8331
60	·8956	87	·8305
65	·8840	88	·8279
68	·8769	89	·8254
70	·8721	90	·8228
72	·8672	91	·8199
74	·8625	92	·8172
76	·8581	93	·8145
78	·8533	94	·8118
79	·8508	95	·8089
80	·8483	96	·8061
81	·8459	97	·8031
82	·8434	98	·8001
83	·8408	99	·7969
84	·8382	100	·7938

TABLE OF THE SYMBOLS AND COMBINING WEIGHTS OF THE MOST COMMON ELEMENTS.

Name.	Symbol.	Comb. Weight	Name.	Symbol.	Comb. Weight.
Aluminium	Al	27·4	Lead	Pb	207
Antimony	Sb	122·0	Lithium	Li	7
Arsenic	As	75	Magnesium	Mg	24
Barium	Ba	137	Manganese	Mn	55
Bismuth	Bi	210	Mercury	Hg	200
Boron	B	11	Nickel	Ni	58·7
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112	Oxygen	O	16
Calcium	Ca	40	Palladium	Pa	106·6
Carbon	C	12	Phosphorus	P	31
Chlorine	Cl	35·5	Platinum	Pt	98·7
Chromium	Cr	52·2	Potassium	K	39·1
Cobalt	Co	59	Silicon	Si	28
Copper	Cu	63·5	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Strontium	Sr	87·5
Hydrogen	H	1	Sulphur	S	32
Iodine	I	127	Tin	Sn	118
Iridium	Ir	198	Uranium	U	120
Iron	Fe	56	Zinc	Zn	65·2

A CORRECTION.

At page 71 of this work it is stated that in Mr. H. Cooper's two formulæ for emulsions, the silver nitrate "is in defect." This is correct as regards the first formula, but (as Mr. Cooper has kindly pointed out) is not the case in the second. In this last there is, in reality, an excess of at least three grains of free silver nitrate.

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$7\frac{1}{2} \times 5$ ...	4 10 0	„ 1 3 6
$8\frac{1}{2} \times 6\frac{1}{2}$ ...	4 17 6	„ 1 7 0
10 × 8 ...	5 10 0	„ 1 12 0
12 ×10 ...	6 10 0	„ 2 0 0

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3 ...	12×10 ...	10×8 ...	$13\frac{1}{2}$in. ...	12 10 0
4 ...	15×12 ...	12×10 ...	$16\frac{1}{2}$in. ...	16 10 0
5 ...	18×16 ...	15×12 ...	20 in. ...	25 0 0
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,, 7	9 ×7	10×8	12×10	9in.	7 0
,, 8	10×8	12×10	13×11	10in.	8 0
,, 9	12×10	13×11	15×12	12in.	9 0
,, 10	13×11	15×12	18×16	15in.	10 0
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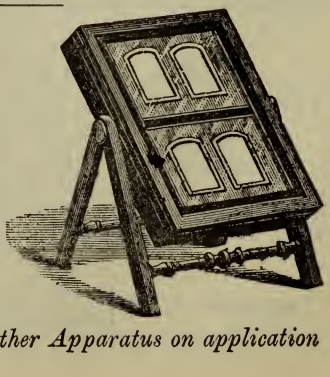

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